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THE SIMULATION AND WATER QUALITY CHARACTERIZATION OF A COAL SLURRY INVOLVING EASTERN COAL

BY

MICHAEL R. TODD
B.S.E., University of Central Florida, 1982

THESIS

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ABSTRACT

The water quality characteristics of a coal slurry were found to vary widely, depending upon the coal used and the use of a corrosion inhibitor. The coal-water interactions were evaluated in a pilot-plant closed-loop coal slurry pipeline. Pulverized coal from eastern Kentucky and tap water were slurried and pumped through a 40 foot (12.2 m) pipe loop for ten days. Slurry samples were collected at 3 hours, 7 hours, 1 day, 2 days, 4 days, 7 days and 10 days from the start of a run. The samples were filtered and analyzed for 29 water quality parameters, including 15 metals. Two runs were performed without adding a corrosion inhibitor and two runs were performed with the addition of a corrosion inhibitor.

The coal slurry filtrate contained high levels of sulfates, total dissolved solids, conductivity, acidity, iron, magnesium, manganese, lead and aluminum. The pH dropped initially, depending upon the percent sulfur in the dry coal and the alkalinity in the slurry, but returned to 6-7 after 10 days in the pipeline. Metal concentrations were a function of the pH, which affected solubilities. Organics in the filtrate were at low levels. The addition of a corrosion inhibitor increased the concentrations of most parameters.

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CHAPTER I

INTRODUCTION

As reserves of oil and gas are becoming depleted, America is turning to other sources of energy. The use of coal is expected to increase substantially in the near future. The U.S. is fortunate to have vast coal reserves located in both the eastern and western states. This coal, however, must be transported from the mines to the major energy consuming areas of the country. Economics is an important factor in coal transportation.

Coal slurry pipelines have been shown to be an economically competitive means of transporting coal. One 440 km (273 mile) coal slurry pipeline has been in continuous operation since 1970 and transports coal from mines in Black Mesa, Arizona to the Mohave Generating Station in Nevada. Several proposed pipelines are in the planning stages of development. These pipelines are planned for both the eastern and western states.

One main drawback to coal slurry pipelines is the amount of water required to act as the carrier medium. Coal slurries will be 50% water by weight which will result in the loss of billions of gallons of water per year from the coal mining states. Some of these states are in water poor areas and the losses could have substantial effects.

A problem also exists in discharging the excess water at the pipeline terminus. Most likely, the excess water will be used as

cooling tower makeup water at the power plants. The remaining water must still be discharged, however, and must meet environmental quality criteria.

Coal contains many contaminants. Coal to be transported in slurry pipelines will be pulverized to very fine particles before mixing with water. This will allow a tremendous surface area of coal to be contacted with the slurry water. The coal and water will be agitated for up to 10-12 days in the pipeline (depending on pipeline length) in an environment of high pressure and possible increased temperature. Thus, many coal-water interactions could occur.

The environmental impacts of the pipelines are predictable, but the water quality and the impacts at the discharge points are not well known. Several studies have been done by researchers at several universities across the country to determine the water quality characteristics involved with coal slurry pipelines. It has been found that the water quality is dependent upon coal sources and water sources for the slurries. Coals from the western U.S. differ greatly from eastern coals with eastern coals typically having higher sulfur content and less alkaline metals in the ash. Even coals from the same area or same mine can differ. Water sources vary from surface water to fresh or saline groundwater, or possibly municipal wastewater. Therefore, each slurry is unique and results in unique water quality characteristics.

Most of the previous water quality studies have been performed using western coals. Thus, there is a need for research using eastern coals. The project based at the University of Central Florida was performed to satisfy this need. The coal for this project originated from mines in eastern Kentucky. The coal was shipped by rail to the McIntosh Power Plant in Lakeland, Florida from which UCF obtained samples of the pulverized coal. The coal was typical of an eastern bituminous coal.

Also, unique to the UCF project was the use of a pilot plant closed-loop coal slurry pipeline to conduct the testing. The purpose of the pilot plant was to simulate an actual coal slurry pipeline system. In an actual pipeline system, the coal and water are slurried, stored in agitated tanks, pumped through the pipeline, stored at the pipeline terminus, and separated by centrifugation. The pilot plant system involved an agitated "storage" tank from which the slurry was continuously pumped through the pipeline and back into the tank in a closed-loop pattern. Samples were withdrawn from the pipeline at regular intervals up to ten days from the start of the test run. The ten-day duration period was selected to approximate the time of transport in long pipelines. The samples were filtered and the filtrate was analyzed for various water quality parameters. The change of each parameter with time was observed and reported.

Tap water was used as the slurry medium. The water originated from local groundwater and was aerated and chlorinated prior to use.

Two slurry runs were performed using plain tap water and two runs were performed with the addition of a corrosion inhibitor to observe any differences in water quality behavior. A description of the project and the results obtained are presented in the following chapters.

CHAPTER II

LITERATURE REVIEW

Although the idea of coal slurry pipelines is not new, very little data is available on the expected water quality at the pipeline terminus. As previously mentioned, research in this area has been conducted recently at a few sites across the U.S. In the following sections, several of these studies are reviewed.

Southern Utah State Analysis

The only chemical analysis of a commercial operating coal slurry pipeline was done by the Southern Utah State Water Laboratory during November 1-10, 1976 for the U.S. Bureau of Land Management (1). The Black Mesa Pipeline is an 18 inch (45.7 cm) diameter, 273 mile (439 km) pipeline from the Black Mesa Mine in Arizona to the Mohave Generating Station in southern Nevada. Samples of Black Mesa well water and slurry arriving at the Mohave Generating Station were analyzed for a number of inorganic parameters. The slurry was centrifuged and then passed through 0.43 micron filters. Table 1 shows the concentrations of various parameters in the well water and in the slurry. Most parameters increased considerably. Nitrate, zinc and arsenic decreased.

The Black Mesa slurry flows at a velocity of 5-6 feet per second, which allows a detention time of three days in the pipeline. The

TABLE 1

RESULTS OF BLACK MESA PIPELINE SLURRY ANALYSES
(Concentrations in mg/l except where otherwise noted)

Water Quality Parameter	Black Mesa Well Water		Coal Slurry at Mohave Plant Intake[a]
	SUS[a]	USGS[b]	
pH[c]	8.45	8.48	9.01
Alkalinity	93.1	77.5	829
Total Hardness	22	15	72
TDS	148	136	1,392
Sulfate	15.5	17.5	132
Nitrate	0.22	1.2	0.020
Chloride	13.8	3.2	81
Magnesium	1.2	0.05	3.7
Potassium	0.54	0.75	5.75
Sodium	46	40.5	454
Aluminum	<0.01	ND[g]	0.54
Lead	<0.001	0.009	0.06
Silica	14.9	21.5	15.7
Electrical Conductivity[d]	138	250	2,191
Turbidity[e]	0.85	ND	40,000
Calcium	6.9	6.0	22.8
SAR[f]	4.2	6.4	23
Arsenic	0.007	0.003	<0.001
Cadmium	<0.001	0	0.014
Copper	<0.001	0.0015	0.011
Iron	0.065	0.045	0.53
Molybdenum	0.020	0	0.06
Nickel	<0.001	ND	0.015
Silver	0.005	ND	0.005
Zinc	0.006	0.020	0.004
Mercury	0.003	<0.00005	0.001
Total Phosphorus	0.090	ND	0.55

[a] Data provided by Southern Utah State Water Laboratory, Southern Utah State College, Cedar City, Utah. Test performed November 1-10, 1976.

[b] Data provided by U.S. Geological Survey Water Resources Division, Flagstaff. Tests performed November 17, 1976. Values reported here are averages of results for two wells.

[c] pH units

[d] micromhos/cm

[e] Jackson Turbidity Units

[f] Calculated

[g] No data

SOURCE: Anderson et al. (1)

coal is ground and held in agitated storage tanks before transmission. The coal has a sulfur weight percent of 0.40.

UCLA/SAI Project

Orson L. Anderson, of the University of California, Los Angeles, and Michael B. Rogozen, of Science Applications, Inc., conducted experimental work on coal slurries from February to May, 1978. They conducted controlled laboratory experiments using Utah coal (1). The feasibility of low quality water was explored by using primary-treated sewage effluent and saline water for the slurry media.

The coal was from the Wasatch Plateau Coal Field in Utah and was bituminous with a sulfur content of 0.64% by weight. It was crushed, ground, and sieved to give a size distribution comparable to that used in the Black Mesa Pipeline. Slurry media used were distilled water (deionized and membrane filtered), unchlorinated primary-treated sewage effluent, and an artificial saline solution.

Polyethylene carboys were used to contain the slurry analyzed for inorganics. Glass carboys were used for slurry to be analyzed for organics. The liquid media was added first and dissolved oxygen was stripped with nitrogen. Coal was then added to give a 50% slurry by weight. A small stainless steel mixing rod helped to wet the coal until a carboy was filled. The polyethylene carboys were sealed with silicone corks wrapped in Teflon tape. The corks were then heavily wrapped with ducting tape.

The carboys were placed on a roller table driven by an electric motor. Tbe twenty-liter slurry carboys were allowed to rotate at about 20-25 revolutions per minute. The glass carboys broke after three days and the coal/distilled water slurries were lost. In their place, 500 ml Teflon jars were filled with new 26.5% solids slurry mixtures and the tops were sealed with Teflon tape to prevent leakage. The jars were placed on a shaker table and agitated for seven days, after which they were removed and refrigerated at 4°C until filtration. The polyethylene carboys were removed from the roller table after ten days and refrigerated.

The slurries for inorganic analyses were vacuum filtered through 0.4 micron Nucleopore filters. The filtering rate was so slow, averaging 1.0 to 1.5 liters per hour, that the remaining slurry was centrifuged at 2500 rpm for 15 minutes to remove a majority of the coal before filtering. The filtrates of all samples were preserved with HNO_3 and refrigerated.

The coal/distilled water mixtures were to be analyzed for organics. They were centrifuged at 2500 rpm for 15 minutes and the supernatant was vacuum filtered through 0.3 micron glass fiber filters.

Samples of coal analyzed for organics were extracted with a mixture of toluene and methanol and with pyridine, in order to separate coal constituents into more readily analyzable groups. The toluene-methanol extract yielded hydrocarbon waxes, elemental sulfur, and

inorganic salts, whereas the pyridine extract showed greater recovery of phenols. The total extracts measured 116 mg/g coal and 48 mg/g coal for the toluene-methanol and pyridine extracts, respectively. Liquid column chromatography was done on these extracts. Compounds identified were straight-chain hydrocarbons, phytane, alkyl-substituted naphthalenes, and phenols.

The filtrate from the coal/distilled water mixture was also fractionated by liquid column chromatography. The results were similar to those for the whole coal, except the filtrate showed greater complexity and had a larger percentage of unresolvable compounds in higher molecular weight regions. Gas chromatography-mass spectometry analysis of the benzene fraction identified at least twelve alkyl-substituted naphthalenes, of which dimethyl naphthalene was the most prominent. Some three-ring aromatic hydrocarbons (anthracene and phenanthrene) and a five-ring heterocyclic compound (flouranthrene) were also identified. Gas chromatograph data indicate that concentrations of aromatics and hydrocarbon waxes in the filtrate were about 2.3 and 0.83 ppm, respectively. Indirect evidence from the GC analysis indicates that the slurried coal was subjected to more oxidative weathering and/or microbial degradation than was the whole coal, which probably occurred during grinding and/or slurrying.

The inorganic parameters were measured using procedures specified in Standard Methods (2). Metals were determined by atomic absorption spectrophotometry. Table 2 summarizes the results of the UCLA laboratory analyses.

TABLE 2

CHEMICAL CHARACTERISTICS OF PRIMARY EFFLUENT AND COAL/PRIMARY EFFLUENT SLURRY FILTRATE (mg/l, EXCEPT pH)[a]

Constituent[b]	Primary Effluent Before Slurrying (without coal)	After 10-day Suspension	
		Primary Effluent (without coal)	Coal/Primary Effluent Slurry
pH	7.5	7.3	6.9
Alkalinity (as $CaCO_3$)	290	140	50
Hardness (as $CaCO_3$)	540	500	540
Total filtrable phosphate (as P)	5.6	1.2	<0.003
Sulfate (as SO_4)	470	440	550
Chloride (as Cl)	120	200	180
Chemical oxygen demand	80	30	c
Total filtrable residue	1260	1330	1470
Cadmium	<0.008	<0.008	<0.008
Zinc	<0.004	<0.004	<0.004
Mercury	<0.9	<0.9	<0.9
Lead	<0.06	<0.06	<0.06
Iron	<0.02	<0.02	<0.02
Sodium	163	170	212
Magnesium	55	55	62
Calcium	103	108	90

[a] Filtered through 0.4 μm filters; unfiltered wastewater was used in experiments
[b] Analyses according to Standard Methods
[c] None detected

SOURCE: Margler and Rogozen (3)

The effluent slurry had less than half the alkalinity of the control effluent which was 140 mg/1. The pH decreased slightly to 6.9. Sulfates increased only slightly to 550 mg/1 as the Utah coal was low in sulfur content. Hardness remained stable at 540 mg/1. Phosphate decreased in both the control and slurry, as did the COD, with the slurry dropping to zero. Chlorides and sodium climbed in both solutions to around 200 mg/1. Heavy metals remained very low and were undetectable.

University of Arkansas Project

Dr. James W. Moore, of the University of Arkansas, led a coal slurry project encompassing the period July, 1975 to December, 1978. Wyoming coal from different sources was tested with various types of water sources (4,5).

Coals were obtained from the Wyodak and South Belle Air Mines near Gillette, Wyoming. The coal was ground and sieved to attain a size range typical of full-scale pipelines. Two water sources, distilled and secondary-treated effluent, were added to the coal to obtain a particular solids concentration, 30, 40, 50 or 60%.

Mixing the slurry was accomplished by two twelve-gang stirring devices. The twenty-four vessels were eight inch (20.3 cm) diameter PVC pipe with plexiglass covers on the top and bottom. O-rings were used to seal the top and bottom plates. A stainless steel mixing shaft extending through the top plate was sealed with an O-ring also. A nitrogen blanket was maintained above the slurry in the vessels tested under anaerobic conditions. Aerobic tests were done also.

Following purging of the air from the vessels with nitrogen, each container was unopened until the appropriate mixing time had elapsed. For a typical run, one container was opened after a mixing time of one hour, and one was opened at each succeeding twenty-four hour interval until the run was completed.

Dewatering was accomplished by sequential vacuum filtering through a Buchner funnel using Whatman No. 42 filter paper and through 0.45 micron glass fiber filters.

Analyses were performed according to Standard Methods (2) or Methods for Chemical Analysis of Water and Waste (6). Heavy metals were analyzed by atomic absorption spectrophotometry.

Table 3 summarizes the results for the anaerobic tests. The aerobic data is felt to be not representative of actual pipeline conditions and is, therefore, not presented here. Moore presented the data in graphical form and the values given in Table 3 are estimates from his plots.

For the distilled water tests, total alkalinity for the Wyodak coal, averaging 100 mg/1, was very erratic over the eleven days but ended up close to the original concentration. Alkalinity in the Belle Air slurry showed a steady decrease from about 60 mg/1 to 15 mg/1. Aluminum concentrations climbed slightly for both slurries but remained low. BOD_5 values decreased steadily for both coal slurries from 140 mg/1 to as low as 30 mg/1 for the Belle Air slurry. COD for the Wyodak slurry remained stable except for a pronounced jump to 620 mg/1 at nine days after which the COD fell back down. The Belle

TABLE 3

UNIVERSITY OF ARKANSAS DATA FOR WYOMING COAL
UNDER ANAEROBIC CONDITIONS*

Parameter	Coal	One-Hour	Final
Total Alkalinity (mg/l as $CaCO_3$)	Wyodak	90	110
	Belle Air	58	15
Aluminum (mg/l)	Wyodak	0.95	1.08
	Belle Air	1.02	1.20
BOD_5 (mg/l)	Wyodak	145	105
	Belle Air	135	30
COD (mg/l)	Wyodak	380	345
	Belle Air	180	80
Calcium (mg/l as $CaCO_3$)	Wyodak	220	280
	Belle Air	130	305
Total Hardness (mg/l as $CaCO_3$)	Wyodak	-	-
	Belle Air	180	440
Lead (mg/l)	Wyodak	0.32	0.32
	Belle Air	0.13	0.11
Nitrate (mg/l as N)	Wyodak	0	13.5
	Belle Air	8.8	7.5
pH	Wyodak	5.9	6.7
	Belle Air	5.9	6.0
Potassium (mg/l)	Wyodak	10.6	8.3
	Belle Air	4.5	5.5
Silica (mg/l as SiO_2)	Wyodak	3.2	2.8
	Belle Air	3.5	3.5
Sodium (mg/l)	Wyodak	120	120
	Belle Air	100	90
Dissolved Solids (mg/l)	Wyodak	1200	1100
	Belle Air	1200	1100
Specific Conductance (μmhos/cm)	Wyodak	1750	2100
	Belle Air	1750	1650
Sulfate (mg/l as SO_4)	Wyodak	700	750
	Belle Air	450	400
Titanium (mg/l)	Wyodak	0.45	0.5
	Belle Air	0.75	1.6

* All tests were with distilled water at 40% solids and an eleven-day detention time.

Air COD values decreased linearly. Calcium and total hardness jumped initially after one day and then leveled off in the range of 300 mg/l and 440 mg/l, respectively. Lead concentrations remained exactly at the same low level throughout the eleven day period. Nitrate values for both coals were very erratic over the mixing period, but remained less than 15 mg/l. The Wyodak slurry showed a large increase in nitrate while the Belle Air slurry remained unchanged. The pH for the Belle Air slurry increased above 7.0 and then leveled off. The pH for the Wyodak slurry climbed steadily but erratically to 6.7. Potassium concentrations rose up and down like sinusoidal curves with the Wyodak slurry dropping from above 12.0 to 8.3 on the eleventh day. The silica values were very stable and remained below 3.5 mg/l during the eleven days with almost no change. The same held true for sodium which was in the range of 90 to 120 mg/l. The solids concentrations were fairly stable at 1100 mg/l. Conductance rose slightly from 1750 μmhos/cm for both slurries and then declined after the ninth day. Sulfates climbed and then fell back to the original range of 400 to 700 mg/l. Titanium for the Belle Air coal slurry initially dropped and then climbed after two days to above 1.6 mg/l. The Wyodak slurry's titanium level remained the same at 0.5 mg/l.

Anaerobic tests using secondary-treated municipal wastewater behaved very similarly to the distilled water tests. Therefore, there is no need to present these data here. COD for the Belle Air

wastewater slurry fluctuated more and the final value was close to the initial value. Also, the sulfate concentration for this slurry increased slightly, rather than decreasing slightly as in the distilled water test. The municipal wastewater tests, in general, produced the same behavior as the distilled water tests, but the initial and final concentrations were generally higher due to the initially higher levels in the slurry medium.

Dr. Moore later extended his studies and tested eastern coals and different water sources (7,8). The same procedures were followed as in the Wyoming coal tests. Coals from Illinois and Kansas were mixed with distilled water, surface water, or municipal treatment plant effluent. The results are shown in Table 4. Once again, the beginning and final numbers presented here were estimated from Moore's published graphs. The average values were given directly by Moore. All graphs were shown to be linear.

It can be seen that sulfates climbed rapidly and leveled off after one hour of mixing. The Kansas coal slurry, averaging 2300 mg/l, was higher in sulfates than the Illinois coal slurry, averaging 1400 to 1500 mg/l. Total hardness remained steady for the Kansas slurry but climbed 800 mg/l in the Illinois slurry to give roughly the same average value of 2200 mg/l for both coal types. Chlorides climbed substantially with the Illinois slurry having much higher concentrations up to 1650 mg/l. Sodium remained the same after one hour and the Illinois slurry contained ten times more sodium at 470 mg/l. The same occurred for dissolved solids with the Illinois slurry

TABLE 4

UNIVERSITY OF ARKANSAS DATA FOR EASTERN COALS
(Detention Time = 15 days)

Parameter	Coal	Water	1-Hour	Final
Sulfate (mg/1)	Illinois	distilled	1420	1300
	Kansas	distilled	2250	2250
	Illinois	surface	average 1550	
	Kansas	effluent	2370	2370
Total Hardness (mg/1)	Illinois	distilled	1600	2400
	Kansas	distilled	2250	2150
	Illinois	surface	average 2130	
	Kansas	effluent	average 2230	
Chloride (mg/1)	Illinois	distilled	1350	1650
	Kansas	distilled	20	200
	Kansas	effluent	50	230
Sodium (mg/1)	Illinois	distilled	460	470
	Kansas	distilled	45	50
Dissolved Solids (mg/1)	Illinois	distilled	6300	6350
	Kansas	distilled	3600	3650
	Kansas	effluent	average 3600	
BOD_5 (mg/1)	Illinois	all	too low to measure	
	Kansas	distilled	average 58	
	Kansas	effluent	average 45	
COD (mg/1)	Illinois	distilled	average 26	
	Illinois	surface	average 17	
	Kansas	distilled	average 93	
Alkalinity (mg/1)	Illinois	distilled	average 10	
	Illinois	surface	average 8	
	Kansas	distilled	average 18	
	Kansas	effluent	average 27	
Fluoride (mg/1)	Illinois	distilled	average 1.61	
	Illinois	surface	average 1.56	
	Kansas	distilled	average 1.54	
	Kansas	effluent	average 1.96	

TABLE 4 (Continued)

Manganese (mg/1)	Illinois	distilled	2.3	1.3
	Kansas	distilled	average	2.3
	Kansas	effluent	average	3.0
Potassium (mg/1)	Kansas	distilled	average	11.1
	Kansas	effluent	average	13.4
	Illinois	distilled	average	38
Nickel (mg/1)	Kansas	distilled	average	0.75
	Kansas	effluent	average	1.13
	Illinois	distilled	0.48	0.30
Lead (mg/1)	Kansas	distilled	0.21	0.20

showing concentrations as high as 6300 mg/1. The Kansas coal slurry exhibited BOD_5 and COD values of 50 mg/1 and 90 mg/1, respectively, and the Illinois slurry remained very low for both values. Alkalinity was at 20 mg/1 or lower for both slurries. Nominal amounts of fluoride and manganese were present. The Illinois coal slurry contained three times as much potassium (averaging 38 mg/1) as the Kansas slurry. Nickel was high enough in the Kansas slurry to require treatment, if discharged. Lead was shown to be 0.20 mg/1 in the Kansas coal slurry. The pH was measured and remained unchanged in all tests. The pH values were in the range of 7.0 to 7.9 in slurries prepared with the Kansas coal.

University of Missouri Project

Manahan, Godwin and Shinn completed a project encompassing the period October 1, 1978 to January 30, 1980 at the University of

Missouri (9). They investigated the leaching of metals and organic matter from sub-bituminous coal and lignite under simulated coal slurry pipeline conditions. Laboratory tests were performed rather than building a reactor or pipeline system.

Sub-bituminous coal from the Powder River Basin of Wyoming and lignite from North Dakota were sampled and analyzed for metals concentrations. Table 5 shows the metals analyses of the coals used for slurries.

TABLE 5

WATER QUALITY FOR 50% SLURRY AFTER 24 HOURS

Parameter	Sub-bituminous coal		Lignite	
	in water	in coal	in water	in coal
pH	4.34		3.50	
Acidity, meq/l	not given		5.31	
COD, mg/l	300		2230	
Metals, ppm:				
Li	0.070	6.2	0.340	2.6
Na	181.2	570	315.8	1,200
K	8.98	435	8.08	440
Mn	2.68	53	8.70	147
Mg	300.0	2,110	856.2	6,240
Ca	553.0	11,130	531.0	18,740
Fe	0.400	4,980	2.35	14,440
Cu	0.047	44	0.57	17.3
Zn	0.156	49	0.207	16.5
Al	1.63	13,110	8.62	6,420

For slurry preparation, both coal types were stored in closed containers in contact with air at 100% relative humidity prior to processing. The coal was reduced in size in a blender such that 75% of the solids were in the 200-20 mesh size range and 25% were less than 200 mesh. Distilled water was used for the makeup water. Slurries with a total volume of 100 ml were prepared ranging from 0.1 to 50% coal by weight. These slurries were sealed in conical flasks and shaken on a shaker table for 24 hours. The water and solids were separated by centrifugation for one hour. The water was separated and analyzed for metals, COD, acidity, and pH. Samples for metals analysis were acidified with HNO_3 and analyzed by flame atomic absorption. Acidity was determined by potentiometric titration in a nitrogen atmosphere.

Most parameters measured higher in the lignite coal slurries than in the sub-bituminous coal slurries. This was due to higher concentrations in the coal. The pH was very low for both coals. The pH declined quickly as the percent solids was increased and leveled off around 4.0 at 30% coal in the slurry. The acidity for the lignite coal slurry increased linearly as percent solids was increased. The COD values jumped up at two percent coal and then steadily increased after falling back down. The COD of the lignite coal slurry was much higher, at 2230 mg/l, than that of the sub-bituminous coal slurry. Three types of behavior occurred in the metals data when the percentage of coal in the slurries was increased.

A linear climb was evidenced in lithium, sodium, and potassium. Manganese, magnesium and calcium climbed quickly and then leveled off. A third type of behavior occurred for iron, copper, zinc, and aluminum. Such plots showed a sharp peak at two to three percent solids after which the concentrations fell back down and then steadily increased.

The metals were not leached appreciably into the water, despite their significant levels in the coal. The most easily leached metal was sodium, followed by magnesium. It should be noted that these were 24 hour tests and water quality characteristics for longer detention times cannot be easily predicted from this data.

Montana State University Project

Peavy, Jennings and Murgel of Montana State University conducted an experimental project (10, 11, 12) during the period October 1, 1978 to December 12, 1980. A bench scale reactor was used to test a 50/50 coal slurry mixture of Montana coal and dechlorinated tap water. Slurries using saline water were also investigated. A pilot plant pipeline loop was set up but was abandoned due to mechanical problems with the slurry pump.

The reactor used, which was 102 cm (40 inches) in length and 38 cm (15 inches) in diameter, was made of PVC pipe with the ends closed with aluminum plates drawn together by tie rods. Baffles were placed in the reactor to prevent the coal from packing into a lump and sliding along the bottom. Nitrogen gas was injected to

purge air and to maintain a positive pressure to expel samples. The reactor was rotated at approximately ten revolutions per minute for twelve days. Samples were collected through a 0.64 cm (1/4 inch) sampling port at six hours and twelve hours, and one, two, four, eight and twelve days from the start of the experiment.

After sampling, the slurry was centrifuged, decanted, and filtered through a 0.45 micron filter. The pH was measured on unfiltered slurry immediately after sampling. Conductivity was measured with a conductivity meter at 25°C. Alkalinity and chloride analyses were performed titrametrically while sulfates were measured by the turbidimeter method. Analysis for metals was performed by atomic absorption spectrophotometry.

The Montana coal came from the Rosebud Seam and was ground by roller-crusher and hammer mill before it was placed in 55 gallon drums and sealed. Trace element analysis of the Rosebud coal seam is presented in Table 6. The results of the filtrate analysis are shown in Table 7.

Some of the results of the filtrate analysis included behavior of pH, sulfates, alkalinity and heavy metals. Values of pH dropped approximately two units and then stabilized at about 6.0. Conductivity steadily increased from 200 to 1940 μmhos/cm. Alkalinity initially dropped and then increased significantly to 560 mg/l. Chloride concentrations remained relatively low at 5 mg/l. Sulfates increased immediately by 700 mg/l, with only a slight increase

TABLE 6

TRACE ELEMENT ANALYSES OF ROSEBUD SEAM COAL
(Analyses in Parts per Million, ppm, of Whole Coal, Moisture-Free Basis)

Element	Maximum	Average	Minimum
Antimony	2.55	0.61	0.07
Arsenic	21.30	6.02	0.68
Beryllium	1.91	0.44	0.11
Cadmium	1.510	0.129	0.021
Chromium	31.20	5.37	0.40
Copper	40.3	12.5	4.6
Fluorine	173.0	51.0	4.0
Germanium	16.35	2.64	0.10
Lead	94.0	8.8	1.3
Manganese	404.5	66.1	6.7
Mercury	0.61	0.20	0.08
Nickel	163.5	37.3	1.6
Selenium	6.62	1.29	0.07
Zinc	361.0	49.6	1.7

SOURCE: Peavy (11)

TABLE 7

SOLUBILITY OF INORGANIC CHEMICAL PARAMETERS IN FRESH TRANSPORT WATER

Parameter*	Mix Water	Hours			Days				
		0	6	12	1	2	4	8	12
pH (units)	7.8	6.6	6.0	5.9	5.9	5.8	6.0	6.3	6.2
Electrical Conductivity (μmhos/cm)	197	1190	1190	1220	1430	1430	1680	1420	1940
Alkalinity	97	32	52	75	102	179	290	471	558
Chloride	4.12	4.6	4.6	4.9	5.5	4.7	5.0	4.4	4.3
Sulfate	12	700	860	866	866	866	900	900	960
Arsenic	0.011	0.014	0.014	0.014	0.021	0.013	0.018	0.028	0.026
Chromium	0.0005	0.0010	0.0015	0.0015	0.0010	0.0010	0.0010	0.0010	0.0005
Copper	0.07	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Lead	0.006	0.004	0.036	0.035	0.030	0.020	0.033	0.035	0.045
Manganese	<0.01	0.25	0.34	0.37	0.38	0.45	0.53	0.63	0.66
Mercury**	0.74	0.76	0.30	0.28	0.37	0.12	0.22	0.52	0.30
Nickel	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Sodium	3.0	55	65	66	69	71	68	76	79
Zinc	0.02	0.006	0.04	0.05	0.05	0.03	0.05	0.04	0.04
NO_3	0.4	0.3	0.3	0.5	0.5	0.4	0.5	0.6	0.2
DOC	5	22	29	88[a]	24	63[a]	28	22	20

* All values in mg/l except as noted

** Parts per billion

a There is reason to suspect that these samples were improperly handled and are in error.

SOURCE: Peavy (11)

thereafter. Significant dissolution of metals did not occur and the concentrations were too low to be of concern from a water quality standpoint. A steady increase in sodium occurred from 55 to 80 mg/l. Nitrate values remained at 0.6 mg/l or less.

Dissolved organic carbon (DOC) analysis indicated an average value of 24 mg/l. According to Peavy (10), the solubility of organic carbon is pH dependent with saturation levels in the low 20s at pH values between 6.0 and 7.0. Thus, the DOC values are probably at saturation. It was postulated that the organic carbon was probably in the form of humic and fulvic acids. These acids are precursors of haloforms which are known carcinogens. Peavy suggested that chlorination of this water may present a problem by the formation of THMs.

ETSI Pipeline Project

A private firm, Energy Transportation Systems, Inc., has performed simulation tests to determine the water quality characteristics resulting from coal slurry transport operations (13, 14). They have developed plans for a pipeline to deliver coal from Wyoming to several power plants in Oklahoma and Arkansas. The proposed system will receive sub-bituminous coal from mines in the Powder River Basin area of Wyoming and water for the slurry will be obtained from the Oahe Reservoir in South Dakota. The simulation studies were set up to closely resemble the proposed pipeline.

Coal samples were shipped from the mine site in barrels using sealed plastic bags to prevent oxidation and contamination. Water samples were obtained from test wells drilled in the Madison formation and from the Oahe Reservoir. The coal was dry crushed with hammer mills and dry ground in a rod mill that was purged with nitrogen prior to closing and sealing the cover. The ground coal was then mixed with the water sample for the simulation test. Similar to coal slurry systems, the test apparatus comprised open to air agitated containers to represent agitated storage tanks. The slurry was agitated for five minutes for rod mill simulation and for six hours for storage tank simulation. The slurry was then placed in a bench scale reactor, consisting of a cylindrical nalgene container with a metal pipe inserted through the axis. The cylinder was rotated about its axis on a set of rollers driven by an electric motor. The speed of rotation was adjusted so that the wall of the container traveled at a velocity that roughly equals the flow velocity in a pipeline. The size of the metal pipe insert was chosen to give the same volume to surface area of contact as that in the proposed ETSI pipeline. The coal slurry was placed in the container and nitrogen was injected to fill the air space. The container was rolled for fourteen or fifteen days and the slurry was removed.

To simulate dewatering plant operations the slurry sample was agitated in stainless steel containers initially open to air for six hours. Covers were then placed on the containers and the air was

purged out with nitrogen. The slurry was slowly heated to 180°F and filtered. The filtrate was analyzed for various water quality parameters. Table 8 is a summary of the test results. Various combinations of coal and water sources were tested. It can be seen that the final slurry filtrate composition is greatly affected by both the source water and the source coal.

Sodium and potassium increased substantially to a range of 130 to 400 mg/1. Calcium and magnesium increased up to 566 mg/1 and 328 mg/1, respectively, when using Kerr-McGee coal and decreased to 70 mg/1 and 45 mg/1, respectively when using Black Thunder coal. Chlorides and nitrates remained stable from 3 to 46 mg/1. Sulfates increased markedly in most all tests to final values up to 800 mg/1. Bicarbonate concentrations decreased in every test. TDS increased greatly for each test, up to 1520 mg/1, as did the TOC, up to 130 mg/1. The pH of the source water and the one-day or final samples did not differ much and was in the range of 6.0 to 8.0. The COD and BOD values climbed appreciably from as low as 5 and 2 mg/1 up to 275 and 165 mg/1 for COD and BOD_5, respectively. Metals and priority pollutants were tested but no results are available. ETSI maintains that the simulation studies revealed no priority pollutants and only very low levels of metals (13).

TABLE 8

SUMMARY OF SLURRY SIMULATION TESTS DATA

Test No.	1	2	3	4	5a	5b	6a	6b	6c	7a	7b
Test Sample Data:											
Water Source[1]	M-1	M-1	M-14	Oahe	M-14	M-14	Distilled	M-14	M-17	M-14	M-14
Water Sample	422	422	470	473-1	470	470	-	489-1	489-2	489-1	489-1
Source of Coal[1]	BT	KM	KM	KM	KM	KM	BT	BT	BT	BT	BT
Coal Sample	456-1	456-2	467	467	467	467	490	490	490	490	490
Storage (weeks)	5	5	3	8	14	14	2	2	2	10	10
Storage Conditions[1]								Under Nitrogen		Ground Before Storage	
Pipeline Simulation Time (days)	15	15	15	15	14	14	1	1	1	1	1
Filtering Conditions[1]	Heated N_2 Flush					Heated					
Constituent Concentrations:											
Cations (mg/l as $CaCO_3$)											
Sodium and Potassium											
Source Water	86	97	8	177	5	9	0	5	7	5	5
Filtrate	195	181	130	171	127	142	209	309	323	403	345
Increase	109	84	122	-6	122	133	209	304	316	398	340
Calcium											
Source Water	188	188	230	153	210	193	0	235	285	235	235
Filtrate	268	500	338	320	510	565	33	70	80	170	85
Increase	80	312	108	167	300	372	33	-165	-205	-65	-150
Magnesium											
Source Water	107	107	164	103	172	164	0	152	152	152	152
Filtrate	152	295	197	180	328	287	16	45	45	111	49
Increase	45	188	33	77	156	123	16	-107	-107	-41	-103

TABLE 8 (Continued)

Total Cations											
Source Water	381	392	402	433	387	366	0	392	444	392	392
Filtrate	615	976	665	671	965	994	258	424	448	684	479
Increase	234	584	263	238	578	628	258	32	4	292	87
Anions (mg/1 as $CaCO_3$)											
Chlorides and Nitrates											
Source Water	46	46	1	13	1	1	0	3	5	3	3
Filtrate	45	46	7	16	4	3	3	5	3	3	4
Increase	-1	0	6	3	3	2	3	2	-2	0	1
Sulfates											
Source Water	131	130	165	250	156	161	0	160	211	160	160
Filtrate	482	735	404	478	796	783	139	246	293	626	150
Increase	351	605	239	228	640	622	139	66	82	466	-10
Bicarbonate											
Source Water	208	204	231	192	223	198	0	222	220	222	222
Filtrate	87	126	217	171	154	140	106	154	127	43	140
Increase	-121	-78	-14	-21	-69	-58	106	-68	-93	-179	-82
Total Anions											
Source Water	385	380	397	455	380	360	0	385	436	385	385
Filtrate	614	907	628	665	954	926	248	405	423	672	454
Increase	229	527	231	210	574	566	248	20	134	287	69
Total Dissolved Solids (mg/1)											
Source Water	478	458	471	544	433	415	-	476	549	476	476
Filtrate	867	1337	916	903	1406	1520	416	602	625	988	695
Increase	391	879	445	359	973	1105	416	126	76	512	219
pH (Standard Units)											
Source Water	7.6	7.9	7.6	8.3	7.5	7.6	7.0	7.8	7.6	7.8	7.8
Filtrate	7.8	7.8	8.0	7.8	6.6	6.0	8.0	7.9	7.7	7.4	7.8
Increase	0.2	-0.1	0.4	-0.5	-0.9	-1.6	1.0	0.1	0.1	-0.4	0

TABLE 8 (Continued)

Total Cations											
Source Water	381	392	402	433	387	366	0	392	444	392	392
Filtrate	615	976	665	671	965	994	258	424	448	684	479
Increase	234	584	263	238	578	628	258	32	4	292	87
Anions (mg/l as $CaCO_3$)											
Chlorides and Nitrates											
Source Water	46	46	1	13	1	1	0	3	5	3	3
Filtrate	45	46	7	16	4	3	3	5	3	3	4
Increase	-1	0	6	3	3	2	3	2	-2	0	1
Sulfates											
Source Water	131	130	165	250	156	161	0	160	211	160	160
Filtrate	482	735	404	478	796	783	139	246	293	626	150
Increase	351	605	239	228	640	622	139	66	82	466	-10
Bicarbonate											
Source Water	208	204	231	192	223	198	0	222	220	222	222
Filtrate	87	126	217	171	154	140	106	154	127	43	140
Increase	-121	-78	-14	-21	-69	-58	106	-68	-93	-179	-82
Total Anions											
Source Water	385	380	397	455	380	360	0	385	436	385	385
Filtrate	614	907	628	665	954	926	248	405	423	672	454
Increase	229	527	231	210	574	566	248	20	134	287	69
Total Dissolved Solids (mg/l)											
Source Water	478	458	471	544	433	415	-	476	549	476	476
Filtrate	867	1337	916	903	1406	1520	416	602	625	988	695
Increase	391	879	445	359	973	1105	416	126	76	512	219
pH (Standard Units)											
Source Water	7.6	7.9	7.6	8.3	7.5	7.6	7.0	7.8	7.6	7.8	7.8
Filtrate	7.8	7.8	8.0	7.8	6.6	6.0	8.0	7.9	7.7	7.4	7.8
Increase	0.2	-0.1	0.4	-0.5	-0.9	-1.6	1.0	0.1	0.1	-0.4	0

TABLE 8 (Continued)

Total Organic Carbon (mg/1)											
Source Water	5	5	5	8	4	5	0	11	16	11	11
Filtrate	31	37	71	50	96	129	41	41	37	25	40
Increase	26	32	66	42	92	124	41	30	21	14	29
Chemical Oxygen Demand (mg/1)											
Source Water	4	5	6	19	6	9	0	5	5	5	5
Filtrate	109	92	180	137	205	275	84	79	73	50	61
Increase	105	87	174	118	199	268	84	74	68	45	56
Biochemical Oxygen Demand (mg/1)											
BOD (5-day)											
Source Water	-	-	-	-	11	9	0	4	2	4	4
Filtrate	-	-	134	80	140	165	45	43	37	19	52
Increase	-	-	-	-	129	156	45	39	35	15	48
BOD (20-day)											
Source Water	-	-	-	-	14	17	0	-	-	-	-
Filtrate	-	-	173	100	175	216	-	-	-	31	71
Increase	-	-	-	-	161.0	199	-	-	-	-	-
BOD (30-day)											
Source Water	-	-	-	-	17	18	0	-	-	-	-
Filtrate	-	-	284	110	197	240	-	-	-	38	89
Increase	-	-	-	-	180	222	-	-	-	-	-

[1] BT - Black Thunder; KM - Kerr-McGee; stored as shipped from the mine in loosely covered barrels unless otherwise noted. Filtered unheated unless otherwise noted; M - Madison aquifer.

SOURCE: Plummer (13)

Summary of Previous Studies

All research to date has been conducted with bench scale reactors or laboratory containers which have been shaken, rolled, rotated, or stirred. With the exception of the Black Mesa data, no data is available for an actual pipeline. The research performed by the University of Central Florida, utilizing a pilot plant pipeline loop, should provide valuable information on coal slurry characteristics.

From the previous review of the literature on coal slurries, it was seen that the water quality characteristics change with time. One-day data should not be compared with twelve-day data to compare the effects of coals or water sources. The effects of various coals and water sources on the final slurry water quality characteristics cannot be over emphasized. Coals from the same area demonstrated very different characteristics and affected the coal slurries differently.

It was demonstrated by Manahan (University of Missouri Project) that the solids content of a slurry can affect the water quality characteristics, although above approximately 40% solids, the differences are slight (9). It is wise, then, to compare data from one study with another, only if the same solids content was tested.

Anaerobic conditions exist in a pipeline and results from tests done aerobically will vary greatly from anaerobic tests because oxygen affects the chemical reactions which produce the final water quality from the coal and water interface.

Table 9 presents a summary of the results obtained from each coal slurry study. It should be noted that there is much variability between each study. Differences existed between coals, water sources, slurrying methods, sample handling, analytical testing procedures, etc.

In general, as seen in Table 9, the pH seems likely to drop slightly but remain in the neutral range. TDS and conductivity are expected to rise substantially. Alkalinity increases and is higher in the western coals. Chlorides in the slurry water remain the same or increase slightly depending upon the coal. Sulfates increase substantially to a level dependent upon the coal. BOD_5 and COD are very low as shown in most tests. Hardness increases or decreases slightly depending on the coal source. Organic carbon levels attain saturation in slurries. Sodium levels seem to be high in a coal slurry. Heavy metals appear to be low in coal slurries and are dependent upon the pH, which affects solubilities. University of Missouri data showed higher levels of leaching the heavy metals when the pH was very low.

To illustrate variability in research techniques and coals from the same area, the data from the ETSI, University of Missouri, and University of Arkansas studies can be compared for Wyoming coal (see Table 9). Note that the pH values were very different for each study, which would have an effect on the concentrations of most parameters analyzed.

TABLE 9

SUMMARY OF PAST STUDIES FOR SELECTED PARAMETERS

Project	Operating Parameters			Slurry Water Concentrations, mg/l						
	Coal	Water	Detention Time	Sulfate	pH	Alkalinity*	TOC	Fe	Mg	Pb
Southern Utah State	Black Mesa, Arizona	groundwater	3 days	132	9.0	829	-	0.53	3.7	0.06
UCLA/SAI	Wasatch Plateau, Utah	primary effluent	10 days	550	6.9	50	-	<0.02	62	<0.06
University of Arkansas	Wyodak, Wyoming	distilled	11 days	750	6.7	110	-	--	-	0.32
University of Arkansas	Belle Air, Wyoming	distilled	11 days	400	6.0	15	-	--	-	0.11
University of Arkansas	Illinois	distilled	15 days	1300	-	10	-	--	-	--
University of Arkansas	Kansas	distilled	15 days	2250	7.0-7.9	18	-	--	-	0.20
University of Missouri	Powder River, Wyoming	distilled	1 day	--	4.3	-	-	0.40	300	--
University of Missouri	North Dakota	distilled	1 day	--	3.5	-	-	2.35	856	--
Montana State University	Montana	tap	12 days	960	6.2	558	20	--	-	0.045
ETSI	Black Thunder, Wyoming	groundwater	15 days	482	7.8	-	31	--	152	--
ETSI	Kerr-McGee, Wyoming	groundwater	15 days	735	7.8	-	37	--	295	--

* as $CaCO_3$

Based on the data gathered to date, a fair idea of the coal/water interactions exists, but there is a definite need for more research. The University of Central Florida research will help to fill this void.

CHAPTER III

PILOT-PLANT PIPELINE DESIGN AND CONSTRUCTION

The objective of the pipeline loop was to simulate the coal-water processes that occur in actual coal slurry pipelines. However, it had to be small enough to be practical for the research project. Factors considered in the design were ease of construction, reliability, maintainability and cost. A 40 foot (12.2 m) length of 1 inch (2.54 cm) diameter steel pipe was chosen to simulate actual pipeline conditions. Figure 1 is a schematic of the system.

The coal slurry was well mixed in the reactor tank, then pumped out through the upper half of the pipeline where it traveled 40 feet (12.2 m) before returning to the bottom of the tank through an angled nozzle. Figure 2 shows the reactor tank top in detail.

Based on the predicted sample volumes required for water quality testing, a reactor volume of 70 gallons (265 liters) was chosen. This proved to be more than enough for the volume requirements. A cylindrical design for the tank was chosen to provide adequate mixing and ease of construction. The reactor was constructed of 10 gauge (0.14 inch, 0.36 cm) steel.

The top of the tank sides were flanged to provide a suitable support for the top. The top was bolted to the tank with 24 bolts

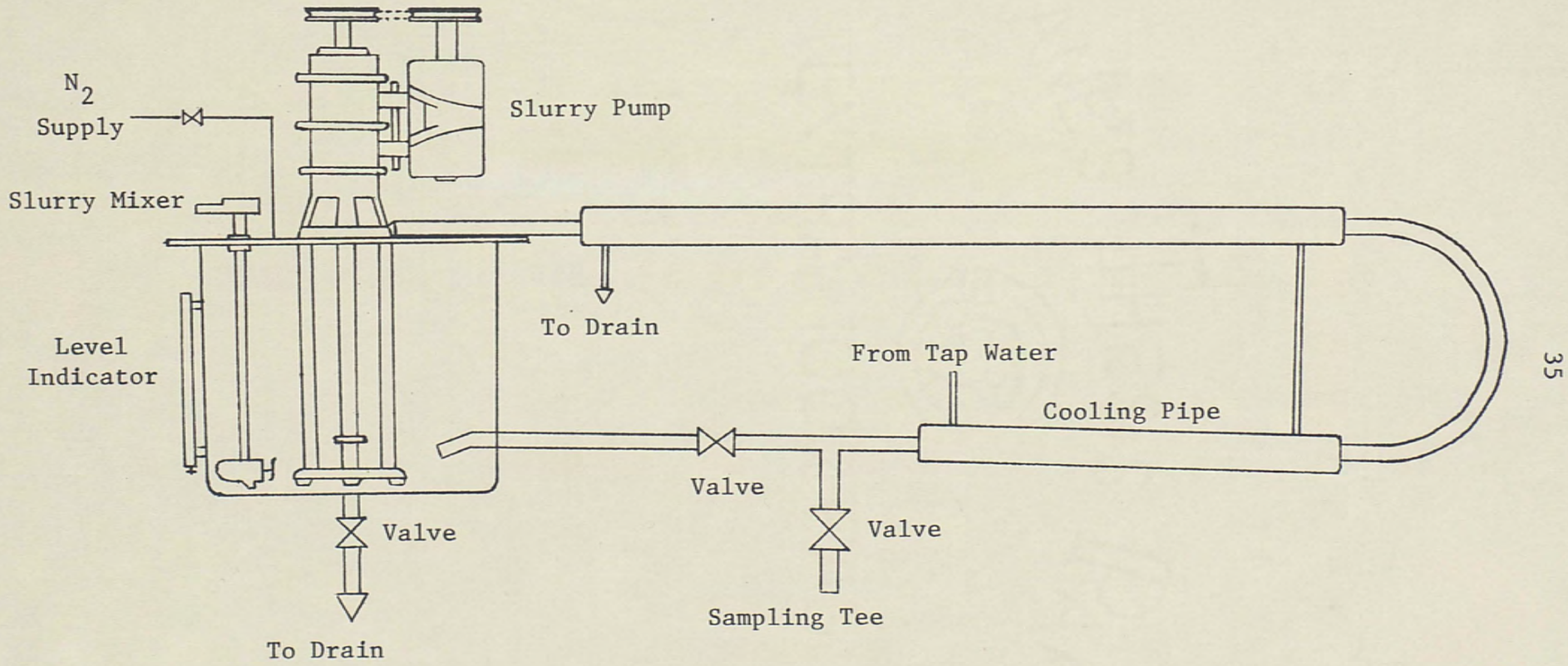

Fig. 1. Reactor and pipeline system.

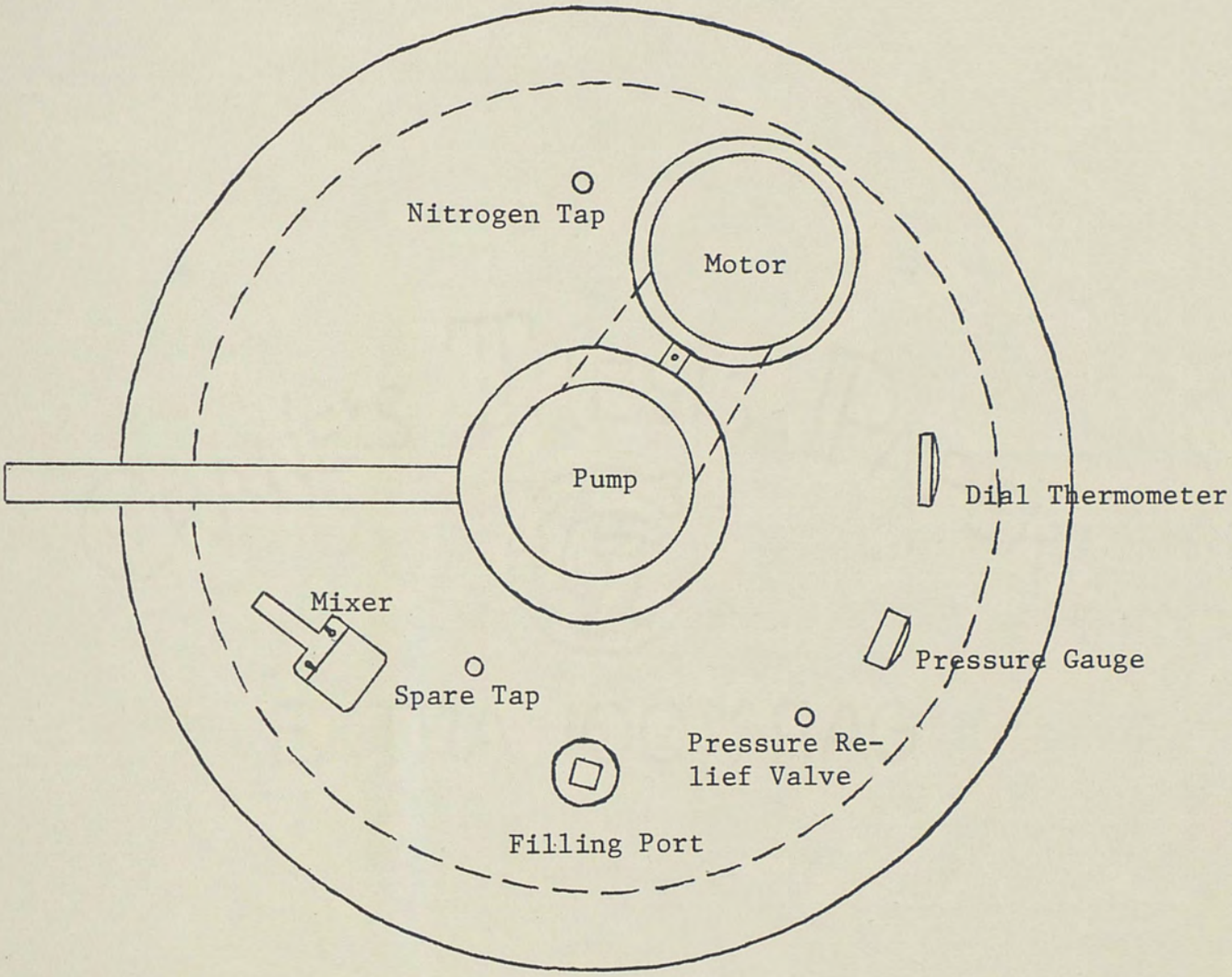

Fig. 2. Reactor tank - top view.

placed around the flange. A rubber gasket was placed in the flange to seal the reactor both from slurry leakage out and air leakage in. Also, to prevent air from entering and affecting the coal-water interactions, the slurry was nitrogen blanketed. Nitrogen gas entered through the tank top via 0.25 inch (0.64 cm) diameter tubing and was pressure regulated. A pressure gauge was installed in the tank top to measure internal pressure; a 1 psi (6895 N/m^2) pressure relief valve was also installed.

The slurry temperature was also a concern and a dial thermometer was mounted on the tank top with a 24 inch (61 cm) stainless steel probe extending down into the slurry. A sight glass/level indicator was installed in the side of the reactor but proved useless when the coal slurry entered it and plugged the bottom valve. The sight glass valves were brass but erosion and possible contamination of the slurry with metals was not expected because the slurry would not be moving quickly through the sight glass. All system valves and pipe unions placed where erosion could occur were cast iron instead of brass.

Another feature of the reactor tank was a drain in the bottom for easy emptying. The tank bottom sloped toward the center and a 1 inch (2.54 cm) diameter steel pipe was welded there. A gate valve was attached to the pipe. A 2 inch (5.1 cm) diameter PVC pipe was fabricated to carry the draining slurry to a floor drain which was connected directly to the neighboring UCF sewage treatment plant.

The tank top was 0.25 inch (0.64 cm) thick steel. Reinforcement angle irons were welded to the underside to help support the weight of the slurry pump. The top featured taps for the nitrogen hose, dial thermometer, pressure relief valve, pressure gauge, and mixer and an extra tap for any unforeseen use. A 2.5 inch (6.4 cm) opening served as a coal slurry loading and tank filling port. All of the openings included galvanized screw caps for sealing the tank when they were not in use.

In the initial design of the pipeline, a tank mixer was optional. It was predicted that the slurry pump, combined with the jet action of the entering slurry through the angled nozzle, would maintain a suspension of the coal solids. However, a sludge developed on the tank bottom during the initial reactor testing with coal slurry. A Shakespeare Model Alpha 12 (12 volt, 15 amp) boat trolling motor was installed due to its availability, size, cost and variability of motor speed. Industrial mixers were much more expensive and, therefore, were not chosen. The trolling motor delivered 12 pounds (53 N) of thrust and provided very good mixing. The propeller was aimed in the direction opposing the flow caused by the incoming slurry from the jet. This allowed better mixing and eliminated the effect of the centrifugal action that could force the solids to the outside edge of the tank where they could settle out. A pipe dressing was welded to the tank top and set screws held the motor shaft in place. It was adjusted up or down while still being sealed properly. The trolling motor was

adjustable for forward and reverse and low or high speed operation. The 12 volt DC motor required a power converter to provide the correct current for continuous operation.

The slurry pump was a submersible Hazleton VNL one-inch model driven by a 1.5 HP (1.1 kw) electric motor (see Figure 1). The pump was belt driven and the pump speed could be varied from 800 rpm to 2400 rpm by an adjustable pulley. The slurry was drawn from the bottom, moved up through the two tubes on the sides, and was discharged out the top. The pump's lower unit was steel and all of the paint was stripped off before installation to eliminate possible contamination of the slurry by metals eroded from the paint. The pump contained no seals which the abrasive coal particles could wear out. It was mounted in the center of the tank top with 12 stainless steel bolts. A gasket was placed between the pump and the top to prevent air leakage.

Occasionally it was necessary to open the reactor to inspect the interior or to install a replacement mixer. To do this the entire tank top along with the pump was raised. This assembly weighed approximately 300 lbs (136 kg). A block-and-tackle was installed directly above the pump and the assembly could be raised out of the tank by two men pulling a rope to the side.

The pipeline was 1 inch (2.54 cm) diameter, schedule 80 steel pipe. Sections were joined by threaded cast iron pipe unions. The pipe extended about 20 feet (6 m) away from the reactor and made a 180° bend to return to the reactor bottom.

Heat exchangers were placed on portions of the pipeline to prevent the coal slurry from getting too hot (see Figure 1). Heat was generated in the slurry by friction caused when the slurry passed through the pump and pipeline. The slurry testing was performed in the summer, therefore, significant temperature rises could occur in the middle of the day which could affect the chemical interactions between the coal and water. To help reduce these large temperature changes, sections of 2 inch (5 cm) diameter PVC pipe were placed over sections of the steel pipeline. The PVC pipe ends were capped and sealed with caulking. Taps were placed in the PVC sections and clear plastic tubing carried tap water from one section to another. The tubing began at a tap water faucet and was routed through the PVC sections and into 0.5 inch (1.3 cm) diameter PVC pipe which was routed to the floor drain. The water flowed slowly in a counter-current direction to the slurry flow within the pipeline. The hottest part of the slurry, coming directly from the pump, was cooled with the warmest tap water.

On the lower half of the pipe loop was the sampling tee (see Figure 1). A valve on the main pipe regulated flow going to the reactor tank and a valve on the short extension opened to let slurry flow out. Both were cast iron gate valves. The valves were placed in a position so that both could be operated simultaneously by one person if all the flow was to be diverted out. Sampling could be performed by simply opening the valve on the extension, since enough pressure was available to push out the slurry.

The supports for the reactor tank and pipeline consisted of a wooden platform, designed to support approximately 1 ton (910 kg), and pipe hangers connected to the roof beams. The research was conducted within an open-sided building with a cement floor. The platform rested on the cement and supported the reactor tank at a height of 3 feet (0.9 m). The nitrogen tank was strapped to the platform. Enough space remained on the platform for one person to stand and make any pump speed or other adjustments. The pipeline was supported by six hangers which were connected to the cross beams in the roof. The weight did not overload the beams as it was evenly distributed (about 30 lbs or 14 kg per hanger). This arrangement allowed a "clean" setup with no ground supports to get in the way.

Auxiliary equipment included a portable platform scale which could weigh up to 1000 lbs (454 kg) and a small electric trolling motor used as a mixer. A 55 gallon (208 liter) drum full of dry coal could be weighed before adding water to obtain a 50-50 mixture by weight. The trolling motor could then mix the coal and water before it was added to the reactor.

At the Lakeland coal-fired power plant, where the pulverized coal was obtained, a unique coal collection apparatus was installed. One of the pulverized coal feed lines to their furnace was tapped and a flexible steel hose was routed into a 55 gallon (208 liter) drum. The drum lid was fitted with two nipples, one for attaching the hose and one for a cloth bag. Pulverized coal, carried by air was blown into the drum; the coal settled and the air exited

through the cloth filter bag. Filling the drum with pulverized coal required approximately two days. The lid could be interchanged with a second drum when the first drum was transported to UCF. Full drums of coal were sealed with a lid and were tightly clamped to prevent any exposure to the atmosphere, rain, etc.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Pipeline Operation

After construction, the pipeline was flushed and filled with tap water to observe the pump operation and test for leaks. Also, between each experimental run, the reactor and pipeline were rinsed with tap water several times to remove any coal remaining in the system. As this rinse water was drained, the reactor tank was filled with nitrogen to prevent internal rusting.

To start a slurry run, the first requirement was to obtain the coal. A 55-gallon (208 liter) steel drum filled with pulverized coal was obtained from McIntosh Power Plant. The drum was sealed to prevent coal dust from escaping, to prevent moisture from entering into the coal, and to prevent excessive oxidation of the coal. The length of time between coal collection and coal slurrying ranged from 1 to 3 weeks.

The drum of coal was then weighed on platform scales, which were calibrated prior to each weighing. The weight of an empty drum was subtracted from the total weight, which gave the weight of the coal only. Tap water was then put into the drum with a plastic hose until the total weight equaled the drum weight plus twice the coal weight. In other words, the weight of the water added equaled the weight of the coal. This gave the desired 50-50 mixture.

In order to mix the coal and water sufficiently, a small mixer (electric trolling motor) was placed in the drum after the weighing. The coal slurry was completely mixed within 20 minutes of the first addition of water.

The slurry was then transferred to the reactor tank. One gallon (3.8 liter) plastic scoops were used to convey the slurry. A funnel was placed in the filling port to avoid spillage. The pump and slurry mixer were started when the tank was half full. If corrosion inhibitor was to be added, it was added at this point to the tank.

When the slurry was transferred, the screw cap was sealed and the tank was pressurized with nitrogen. The nitrogen was then turned off to prevent excessive leakage.

The trolling motor mixer was run at medium speed continuously. The pumping speed was pre-set and was checked during each run. The method for measurement involved a strobe light and a mark on the spinning pulley on top of the pump shaft. The rpm of the pump shaft gave a measure of the pump speed. Prior to the actual slurry runs, the flow through the pipeline was correlated with pump speed. At different pump speeds, slurry was collected from the pipeline sample tee and the increase in the weight of the slurry collected with time was noted. The flow rate in lb/min was converted to liters/minute. The average flow rate used during the testing was 60 liters/minute. This corresponded to a flow velocity in the pipeline of 7 ft/sec (2 m/sec).

At the appropriate sampling time, the temperature of the slurry was noted and the tank was pressurized with nitrogen to displace the slurry removed for samples. The valve on the sampling extension was opened and samples were collected (see Figure 1). The slurry flowed very freely through the pipe and the valve had to be carefully regulated to prevent any slurry loss. After the last sample was collected, the valve was closed and the nitrogen was turned off.

Upon termination of a slurry run, the tank was drained of slurry and filled with tap water. A complete flushing was performed several times until the draining water was clear. The tank and pipeline were filled with nitrogen until the next slurry run.

Slurry Sampling Schedule

It was desired to complete as many experimental runs as could be done within the time period of the project. Two runs were completed without a corrosion inhibitor and two runs were completed with the addition of a corrosion inhibitor.

The corrosion inhibitor is composed mostly of nitrite, borate, and MBT (a proprietary corrosion inhibitor for copper). It was purchased from a commercial water conditioning company. A dose of 1 lb (0.5 kg) per tank provided a residual of 2,000 ppm of inhibitor.

A run consisted of mixing a fresh batch of slurry and pumping it through the pipeline for a 10-day period. Within this 10-day period, samples were drawn according to Table 10.

TABLE 10

SLURRY SAMPLING SCHEDULE

Time after Start of Run	Volume of Sample Taken
3 hours	3.5 liters
7 hours	3.5 liters
1 day	3.5 liters
2 days	3.5 liters
4 days	6.0 liters
7 days	6.0 liters
10 days	6.75 liters + 5.5 gallons (20.8 L)

Volumes taken correspond to the amount needed to perform the analytical testing scheduled for each sampling time. Phenols were tested only on the 4-day, 7-day and 10-day samples. Trihalomethane Formation Potential was performed only on the 10-day samples. The 5.5 gallons (20.8 L) of sample collected on day 10 was required for treatability testing. The treatability testing is not within the subject matter of this thesis and will not be discussed.

Analytical Procedures

Sampling was performed in such a manner as to ensure quality control. Sample containers were as specified in Methods for Chemical Analysis of Water and Wastes, 1974, EPA-625/6-74-003. Glassware and plastic bottles were washed and rinsed with distilled water before use.

In addition, bottles were rinsed with coal slurry before collecting a sample. Bottles for Trihalomethane Formation Potential samples were acid-washed and ashed at 350°C for one hour before use. Containers which were to hold sample destined for metals analysis were acid-washed with nitric acid before use. All sample bottles were filled to the top and allowed to overflow with slurry before capping them.

For the THMFP, TOC and all general parameters, the sample containers were 750 ml Wheaton glass bottles with Teflon screw caps. Samples for metals analysis were collected in 1 liter brown polyethylene bottles with screw caps. Samples for phenols testing were collected in 1 gallon (3.8 L) plastic "milk jugs" which were cleaned thoroughly before use. The water quality parameters measured are listed in Table 11.

TABLE 11

WATER QUALITY PARAMETERS TESTED

General Water Quality		Organics	Metals				
DO	Turbidity	TOC	Ag	Cd	Hg	Pb	Ar
pH	Acidity	THMFP	Cr	Mg	Se	Al	Cu
Color	Alkalinity	Phenols	Mn	Zn	Ba	Fe	Ni
TDS	Chlorides						
Sulfates	Conductivity						
	Redox Potential						

In all tests except DO, pH and redox potential, which all must be measured immediately, the samples were filtered before analysis. Filtering was performed with a 10 inch (25 cm) porcelain filter funnel fitted with 24.0 cm Whatman 1 Qualitative filter paper. The paper

was rinsed with distilled water prior to filtration. Clear filtrate was collected in a one liter flask. Following this rough filtering, a second filtering was performed using a 300 ml Gelman filter funnel with 4.25 cm Whatman GF/C microfiber glass filters, which were pre-rinsed with distilled water, also. Upon final filtering, the sample was returned to the rinsed sample collection bottles. Filters were changed after each liter of filtrate and between each group of samples.

Filtrate for metals analysis was acid preserved. The filtrate was refrigerated until analysis was begun, which was based on time limits recommended by Methods for Chemical Analysis of Water and Wastes. An analysis schedule is presented in Table 12 and a detailed procedure for each test is presented in the following paragraphs.

TABLE 12

ANALYSIS SCHEDULE

Order of Testing	Maximum Time Between Collection and Analysis
1. DO	10 minutes
2. Redox Potential	10 minutes
3. pH	20 minutes
4. Phenols	2 hours
5. Acidity	3 hours
6. Alkalinity	3 hours
7. Color	5 hours
8. TOC	24 hours
9. Conductivity	24 hours
10. Sulfates	7 days
11. Chlorides	7 days
12. Turbidity	7 days
13. TDS	7 days
14. THMFP	3 weeks (chlorination 1 wk)
15. Metals	2 months

General Water Quality

Dissolved Oxygen

A YSI Model 57 oxygen meter was used to measure DO, which is capable of measuring as low as 0.05 ppm dissolved oxygen. The meter was calibrated prior to each test by recording the temperature and measuring the DO at an agitated air-water interface. The unfiltered coal slurry samples were poured into a BOD bottle carefully to avoid aeration. A probe, with stirrer, was inserted and dissolved oxygen was read from the meter after about 10 minutes to let the reading stabilize. The samples were then poured back into the original container to be filtered. After filtering, these samples could be analyzed for other parameters.

The DO test was run twice. Each time a different sample, from a different container, was measured.

pH

pH was measured electrometrically as stated in section 424 of the 14th edition of Standard Methods for the Examination of Water and Wastewater, hereafter referred to as Standard Methods (2). A Corning Model 12 Research pH meter was standardized before each test with pH 7.00 buffer solution. The unfiltered samples were poured into a 250 ml beaker for testing. pH was measured immediately following redox potential measurement on the same sample, which was performed within 10 minutes of sample collection. This small portion of sample,

approximately 100 ml, was discarded. pH was measured on two samples originating from two separate containers.

Color

Color was measured by Bausch and Lomb Spectronic 70 spectrophotometer at a wavelength of 460 nm using 10 cm cells. A set of standards was measured before testing and a standard curve was drawn. Absorbance for the samples was then compared against the curve to obtain color in cpu.

The samples were filtered once before transferring to the lab for color measurement. An iron precipitate formed in the samples, more so in the 1-day and later samplings, during the time between initial filtration and transportation to the lab (approximately 4 hours). This precipitate must be removed to measure true color. Color tests performed prior to Run #3 did not remove this precipitate and high values resulted for color. A modified procedure was developed after Run #3 to obtain more accurate results. In the lab, approximately 80 ml of sample were poured into a beaker. This sample was adjusted to pH 3.0 using H_2SO_4 to prevent further precipitation. The sample was then put through a glass microfiber filter and poured into a 10 cm cell. A distilled water blank was used to zero the spectrophotometer between measurements. Absorbance measurements were performed twice on the same 80 ml at pH 3.0. This sample was then discarded.

Turbidity

Turbidity was measured by a Hach 2100 Turbidimeter. The meter was standardized with an 80 JTU Formazine suspension standard cell. Samples were poured into cells and the JTU reading was obtained from the nephelometer. Duplicate readings were made from two separate sample containers. Samples were returned to the containers after measurement.

TDS

Total dissolved solids analysis was conducted according to section 208C of Standard Methods. A 100 ml filtered sample was dried overnight at 105°C. The samples were placed in a dessicator for one hour. A Mettler Model H10 analytical balance was used for gravimetric measurements. TDS was measured twice on the same bottle of sample.

Acidity

Acidity was measured by potentiometric titration as stated in section 401 of Standard Methods. Earlier measurements, Run #2 and before, were made on unfiltered samples. However, when comparing alkalinity measurements on filtered and unfiltered sample, the filtered samples gave much lower values. Acidity and alkalinity were run on filtered samples thereafter.

Exactly 40 ml of sample were titrated to pH 3.7 by the addition of 0.02N H_2SO_4. The hydrogen peroxide treatment, as stated in Standard Methods, was performed to reduce interferences from hydrolyzable

metal ions. Five drops of 30% H_2O_2 were added to each of two beakers of 40 ml samples and the samples were boiled for 3-5 minutes. A green precipitate usually formed during heating. A watchglass cover retained most of the steam vapor given off. After cooling in a cool water bath to room temperature, the samples were titrated to pH 8.3 with 0.1N NaOH. The acidity could then be calculated. These samples were discarded.

Alkalinity

Alkalinity was measured by potentiometric titration as stated in section 403 of Standard Methods. Exactly 40 ml of filtered sample were titrated to pH 3.7 with 0.02N H_2SO_4. According to Standard Methods, pH 3.7 is the endpoint for titration of industrial wastes or complex systems. Following alkalinity measurement on the samples, acidity was measured on the same 40 ml aliquot to minimize sample volumes required for collection. The titration to pH 3.7 is a preliminary step in the acidity test.

Chlorides

Chlorides analysis was conducted according to section 408A of Standard Methods. Two 20 ml samples of slurry filtrate from the same container were diluted to 100 ml. The samples were adjusted to pH 7-10 with NaOH. A precipitate usually formed and it was filtered out by glass microfiber filters. An indicator solution (K_2CrO_4) was added to the samples and they were titrated with silver nitrate to a pinkish yellow endpoint. H_2O_2 may be added to remove interferences

from sulfide and sulfite ions but no difference was observed. Iron may mask the endpoint but this was not evidenced.

Conductivity

Conductivity was measured with a YSI Model 32 conductivity meter. The filtered samples were poured into 250 ml beakers and heated to 25°C. The conductivity probe was inserted and after approximately 3 minutes the meter stabilized and conductivity could be read. The temperature was maintained at 25°C and the sample was stirred during the stabilization period. The samples were returned to the original container after testing since no contamination had occurred. Conductivity was measured on two separate sample bottles.

Sulfates

Sulfate analysis was done as stated in section 427C of Standard Methods. The turbidimetric method was chosen because it was least susceptable to interferences. The range of sulfate concentrations which allows the method to be used with accuracy is 0-40 mg/l. Since the coal slurry sulfate concentrations were much higher than this, a 1:100 dilution was necessary to fit the concentration within this range.

Initially, sulfate standards, made from H_2SO_4, were analyzed and a standard curve was drawn using a least-squares method, best-fit line. One ml of each sample was pipetted into a 250 ml erlenmeyer flask and 99.0 ml of deionized water were added. As with the standards, 5.0 ml of conditioning reagent were pipetted into the flask.

This reagent was kept well mixed because the ingredients could separate and form layers causing an improper pipet extraction. Then, exactly 0.3 ml of $BaCl_2 \cdot 2H_2O$ crystals were added and the solution was stirred at a pre-set mixing speed with the same size stirring bar for exactly one minute. The $BaCl_2$ crystals reacted with the sulfates to form $BaSO_4$ precipitate. The turbidity was then measured on a nephelometer, Hach 2100 turbidimeter, every 30 seconds for four minutes. The readings usually climbed and leveled off after three minutes. The turbidity was compared against the standards to obtain the concentration of sulfate. Since the samples were diluted 1:100, no turbidity in the original sample could interfere. Sulfates were measured from two separate sample bottles each time.

Redox Potential

The reduction-oxidation potential of the coal slurry water was measured with an Orion platinum redox electrode (Model 96-78). The electrode was attached to the Corning pH meter. The redox potential was measured immediately after sample collection. Approximately 100 ml of unfiltered slurry were poured into a beaker and the electrode was placed in the slurry. After a stabilization period of 90 seconds, the potential was read from the pH meter on the mV scale. An electrode reference filling solution was used which was intended for high molar solutions. This reference solution contained a high concentration of chlorides which may have leaked into the sample. For this reason, the sample was discarded after redox potential measurement. Redox potential was measured from two separate sample containers.

Organics

TOC

Total organic carbon was analyzed using a Beckman Model 915-B TOC analyzer following the manufacturer's instruction manual. A set of standards, 0, 10, 50 and 100 ppm, were tested and a calibration curve was drawn each time the machine was set up. The machine measured total carbon, TC, and inorganic carbon, IC, on separate channels and separate injections were required for each value. TOC could be obtained by subtracting IC from TC. A 200 µl sample was injected until the peaks on the chart paper were consistent. The peaks were then compared against the standard curve to obtain a value of TC and IC. Duplicate measurements were observed from the same aliquot of sample by using two different peaks on the chart. New standards were made up about every 30 days and were stored in a refrigerator. To obtain CO_2-free water for the standards, water was collected immediately after it was boiled in a distilled deionizer apparatus.

THMFP

Trihalomethane formation potential analysis was conducted according to the liquid/liquid extraction procedure listed in the Supplement to the 15th Edition of Standard Methods for the Examination of Water and Wastewater: Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency (15). Samples were chlorinated and the THM's that formed were measured by a

Hewlett-Packard Model 5750 Gas Chromatograph. It was determined from studies on the coal, using different chlorine dosages, that a residual should be evident after 48 hours for a dose of 5 mg/l. This chlorine dosage is practical in terms of actual field applications.

Samples were collected in Teflon-capped bottles which had been ashed. Just before chlorination the samples were filtered once. The pH was raised to 8.0 with NaOH since THM's do not form at low pH conditions. After a second filtering through microfiber filters, a chlorine dose of 5 mg/l was added from a stabilized solution of $Ca(OCl)_2$ at low pH. The pH was readjusted to 8.0 and the sample was poured into 150 ml dark glass bottles and sealed with Teflon caps. The samples were incubated at room temperature for 48 hours away from any light. After the 48 hour period, 10 drops of 0.02N sodium thiosulfate was added to each bottle to dechlorinate the samples. This prevented any further formation of THM's. The samples were then refrigerated until analysis was performed.

The analysis procedure was begun by testing THM standards and obtaining a least-squares method, best-fit standard curve. Ten ml of dechlorinated sample were pipetted into a test tube. Two ml of hexane were then added and the contents of the test tube were well mixed. The THM's were extracted from the sample by the hexane. By injecting the hexane into the gas chromatograph, the THM peaks could be compared against the standard's peaks to obtain the correct

concentrations. Two separate bottles were chlorinated, stored and analyzed to obtain duplicate results.

Phenols

Phenol content was conducted by the 4-aminoantipyrene method, 510A and B of Standard Methods. Sample pH was adjusted to 4.0 and was preserved with 5.0 ml of $CuSO_4 \cdot 5H_2O$. Duplicate 500 ml aliquots were placed in 1 liter Kjeldahl flasks and distilled on a TKN distillation rack. A 450 ml volume of distillate was collected and the sample was cooled. Then, 50 ml of distilled water were added to each Kjeldahl flask. Distillation was begun again and the final volume of the distillate was brought up to 500 ml. Next, 10 ml of NH_4Cl were added to each distillate. The pH was adjusted to 10.0 ± 0.2 with NH_4OH. The 500 ml of distillate were transferred to a 1 liter separatory funnel. To the distillate, 3.0 ml of 4-aminoantipyrene were added and mixed. Color was allowed to develop for 3 minutes. After color development, 20 ml of chloroform were pipetted into the flask. The flask was tightly stoppered and shaken vigorously ten times. The sample was allowed to settle and was shaken again. The extract was collected and filtered through a paper filter and sodium sulfate granules and collected directly in a 5 cm spectrophotometer cell. Absorbance was measured on a Spectronic 70 spectrophotometer against an extracted blank. Then, absorbance was compared against a standard curve to obtain the correct concentration. A blank was run

through each time, along with duplicate samples. Blank preparation involved 500 ml of distilled water and 10 ml NH_4Cl. The pH was adjusted to 10.0.

Metals

Metals were analyzed on an SMI Spectrospan III Plasma Emission Spectrophotometer. The machine was calibrated according to manufacturer's instructions. All samples were acidified to pH 2 with nitric acid. They were transferred from the 1 liter collection bottles to 50 ml disposable polystyrene cups and were covered with Parafilm. Samples were stored in this manner until aspiration was performed. No concentration was done. Standards and blanks were run through first. Then, six samples were aspirated, one at a time. Standards were then run again to check for drift. Multiple sample aspirations were performed when deemed necessary to obtain accurate results. A direct printout was given from the machine for each sample in ppm. Raw data were corrected for drift which was assumed to be linear.

Dry Coal Analysis

The methods used in dry coal analysis are described in detail in Evaluation of Coal Cleaning on Fugitive Elements - Part II, Analytical Methods (16). Tests to be performed were moisture content of solid coal, ash content, total sulfur, heating value, and

trace metals in the coal. Tests conducted at UCF were ash content and trace metals. The other tests were done at the Lakeland power plant where the coal was obtained.

The coal samples were collected from the 55 gallon drum of pulverized coal before water was added. Coal samples were taken from the top and bottom half of the drum to get a representative sampling. Approximately 500 grams of sample were taken from each drum received.

Ash content was measured by placing a weighed sample, in a weighed crucible, into a cold muffle furnace. The temperature was set for 500°C for one hour. The door was opened every 15 minutes during the hour. The temperature was then increased to 750°C for two hours. After the sample had been in the furnace three hours, it was removed, cooled for a few minutes, and placed in a dessicator. When the sample had cooled to room temperature, it was removed from the dessicator and weighed. This weight was compared to the original dry weight to calculate percent ash.

Analysis for trace metals in the solid coal was determined in accordance to the reference stated earlier, but the Plasma Emission Spectrophotometer was used instead of an Atomic Absorption Unit. Samples were ashed and mixed with 40 ml of HNO_3. Samples were placed on a hot plate and digested down to about 6 ml. The volume was brought back up to 20 ml with deionized water. Then, the samples were analyzed on the Emission Spectrophotometer.

All analytical tests were performed by this researcher except TDS, chlorides, phenols, metals and solid coal analysis. These tests were performed by Mr. Mark Flint, a fellow graduate research assistant.

CHAPTER V

RESULTS AND DISCUSSION

The coal slurries tested can be divided into two groups: slurry runs without a corrosion inhibitor and slurry runs with the addition of a corrosion inhibitor. Runs 1, 2, and 3 fall into the first group and runs 4 and 5 fall into the latter.

Run 1 was the first attempt at operating the pipeline, sampling, and performing actual water quality measurements. This run was mainly a learning experience and, although actual measurements were made and data were recorded, the validity of this run is doubtful. Therefore, run 1 data are not presented.

The coal used to make each slurry was analyzed prior to slurrying. The coal used in this study is generally typical of an eastern bituminous coal. Tables 13, 14 and 15 show the observed coal properties. The sieve analysis averaged 70% through 200 mesh.

As can be seen from Table 13, the coal averaged about 16% ash, 35% volatiles, and 49% fixed carbon (dry basis). It had a heating value of about 12,000 Btu/lb and a sulfur content about 1.9%. All parameters varied between each individual slurry run. As shown in Table 14, the ignited ash was primarily silica, alumina, and ferric oxide. As seen in Table 15, major trace metals in the coal were iron, magnesium, barium, manganese, and arsenic. Aluminum was also a major constituent, on the level of iron, but was unable to be measured accurately.

TABLE 13

COAL PROXIMATE ANALYSIS (DRY BASIS)*

Parameter	Run 2	Run 3	Run 4	Run 5	Avg	Composite (as received 18 unit trains, 1981-2)**
% Ash	15.28	14.39	15.37	18.50	15.89	15.11
% Volatiles	32.85	36.79	36.49	35.13	35.32	35.09
% Fixed Carbon	51.87	48.82	47.63	46.37	48.67	49.80
Heating Value (Btu/lb)	11,632	12,830	11,922	11,500	11,971	12,378
%Sulfur	2.26	1.69	1.93	1.70	1.90	2.51

* SOURCE: McIntosh Power Plant Chem. Lab., Department of Elec. and Water Utilities, Lakeland, Florida (17)

** SOURCE: Commercial Testing and Engineering Co., test for McIntosh Power Plant (17)

TABLE 14

TYPICAL MINERAL ANALYSIS OF ASH
(Composite of 18 Unit Trains, 1981-1982)

Component	Weight %, Ignited Basis
SiO_2	49.8
Al_2O_3	24.95
TiO_2	1.14
Fe_2O_3	16.80
CaO	0.90
MgO	1.34
K_2O	2.82
Na_2O	0.30
SO_3	1.65
Other	0.3
Total	100.0

TABLE 15

TRACE METALS ANALYSIS OF COAL

Component	ppm in ignited ash, as the element				
	Run 2	Run 3	Run 4	Run 5	Avg.
Hg	56	47	63	59	56
Se	92	83	72	63	78
Cd	3.5	4.3	4.2	4.2	4.1
Zn	106	311	228	219	216
As	156	238	379	421	298
Mn	163	541	408	505	404
Cu	221	139	154	110	156
Fe	ND*	ND	80,440	73,690	77,070
Pb	122	101	109	104	109
Ni	90	136	133	135	124
Cr	231	133	150	123	159
Ba	585	837	797	720	735
Mg	8490	15,900	8,190	9,610	10,550
Ag	4.0	2.0	7.0	2.5	3.9

* No data

Water used to make up the slurries was tap water obtained from the UCF water supply. This water was pumped from a deep well and was aerated and chlorinated at the UCF water treatment facility. Samples were taken from the hose used to fill the slurry mixing drums. These make-up water samples were analyzed as though they were coal slurry samples. The tap water characteristics are shown in Table 16. In addition, between runs 2 and 3, tap water was added to the cleaned reactor tank, the pipeline was operated for three days, and samples were taken and analyzed for all the parameters. This so-called "field blank" is presented in Table 16. Distilled water was collected in sample bottles and was run through each of

TABLE 16

UCF TAP WATER, FIELD BLANK, AND DISTILLED WATER ANALYSES

Parameter**	Distilled	Field Blank	Tap Water
Sulfates	<2	3.6	< 2
Chlorides	<5	19	19
TDS	34	187	207
Conductivity, µmho/cm	14	262	366
Dissolved Oxygen	8.3	0.7	7.9
Redox Potential, mV	164	203	526
pH, units	5.0	7.2	7.0
Acidity, mg/l as $CaCO_3$	46	-142	-96
Alkalinity, mg/l as $CaCO_3$	2	110	120
Color, cpu	4	5	6
Turbidity, JTU	4.2	0.6	5.3
THMFP, ppb	<5	53.9	131.1
TOC	2	24	14
Phenols	<0.001	*	*
Metals			
Hg	<0.050	< 0.050	0.076
Se	0.121	0.350	0.242
Cd	<0.005	0.006	0.006
Zn	0.021	0.077	0.071
As	0.064	0.057	0.045
Mn	<0.001	0.133	0.009
Cu	0.018	0.018	0.016
Al	0.019	0.167	0.033
Fe	0.100	36.6	1.28
Pb	<0.015	0.039	0.029
Ni	0.006	0.027	0.002
Cr	<0.001	0.005	0.004
Ba	<0.001	0.004	0.015
Mg	<0.001	11.0	11.0
Ag	<0.002	0.006	0.002

* Test was not performed.

**All concentrations are in mg/l unless otherwise stated.

the analytical tests as a check on procedures and sample handling methods. Results are shown for the distilled water blanks also in Table 16.

Table 16 shows that most parameters had low values. TOC was fairly high at 14 mg/l and 24 mg/l for the tap water and field blank, respectively. The negative values for acidity were the result of including the hydrogen peroxide treatment in the acidity analysis. The H_2O_2 treatment is used in the coal slurry analysis to reduce interference from hydrolyzable metals. The tap water, field blank, and distilled water were treated exactly as coal slurry and, therefore, the H_2O_2 treatment was performed. In the acidity analysis, H_2SO_4 was added to the sample to lower pH to about 4.0, H_2O_2 was added, the sample was boiled for about three minutes, and NaOH was added to raise the pH to 8.3. The equivalents of acid added were subtracted from the equivalents of base added in the titration. If the equivalents of acid were greater than the equivalents of base, then a negative value occurred for acidity. When the sample was boiled, CO_2 was lost to the atmosphere which may have lowered the acidity somewhat. The H_2SO_4 added was unable to neutralize the NaOH added later. The H_2O_2 treatment did not affect the distilled water acidity analysis. Acidity tests on the tap water, without including the H_2O_2 treatment, resulted in an average value of 14 mg/l as $CaCO_3$.

It can be seen from Table 16 that the field blank contained much higher concentrations of Mn, Al, Fe and Ni than either the tap

water or distilled water sample. The increased concentrations are probably the result of metals picked up when the water traveled through the pipeline. The coal slurries contained high concentrations of Mn and Fe and a residual was probably left in the pipe which was not completely cleaned.

Table 17 shows the lower detectable limits for each parameter and the limiting factors. Values in Table 16, and in subsequent tables of data, are represented as less than the lower detectable limit when lower values were measured.

Duplicate samples were run for all tests, except metals, and the average values are presented here. Single metals samples were run through the spectrophotometer and the machine automatically aspirated the samples three times and presented the mean and standard deviation to account for machine error. The standard deviations for the general and organics tests were calculated from the duplicate results and the precision was compared with pre-determined objectives. Internal quality control check samples and EPA quality assurance samples were analyzed to determine the accuracy of the analytical testing. All of the parameters were within reasonable ranges except mercury, arsenic and selenium. Analysis of spiked samples, when applicable, also aided in proving the accuracy of the analytical procedures. Tables 18 and 19 are summaries of the analytical and sampling variance. The variances of the metals in Table 19 were calculated from the results of three separate trials at measuring the same samples.

TABLE 17

LOWER DETECTABLE LIMITS

Parameter	Limit	Limiting Factor
Sulfates	2 mg/l	method
Chlorides	5 mg/l	method
TDS	6 mg/l	method
Conductivity	0.1 µmho/cm	instrument
DO	0.1 mg/l	instrument
Acidity	3 mg/l as $CaCO_3$	method
Alkalinity	0.7 mg/l as $CaCO_3$	method
Color	1 cpu	standard curve
Turbidity	0.005 JTU	instr. readability
TOC	2 mg/l	standard curve
THMFP	5 ppb	method
Phenols	1.0 µg/l	standard curve
Metals *	µg/ml	instrument
Hg	0.050	
Se	0.030	
Cd	0.005	
Zn	0.005	
As	0.030	
Mn	0.001	
Cu	0.001	
Al	0.001	
Fe	0.002	
Pb	0.015	
Ni	0.001	
Cr	0.001	
Ba	0.001	
Mg	0.0001	
Ag	0.002	

* Information from the manufacturer based on tests conducted for each individual metal in distilled water. The lower detectable limits for metals in coal slurry matrix may be significantly higher than those listed above.

TABLE 18

SUMMARY OF ANALYTICAL AND SAMPLING VARIANCE
(10-day samples unless noted)

Parameter	Run 2			Run 3			Run 4			Run 5		
	σ[1]	$\bar{X}$[1]	%[1]	σ	$\bar{X}$	%	σ	$\bar{X}$	%	σ	$\bar{X}$	%
General												
Sulfate, mg/l	15	1680	0.9	148	1005	14.7	184	3940	4.7	495	3420	14.5
Chlorides, mg/l	1.4	78.1	1.8	0	154	0	1.4	175	0.8	1.4	180	0.8
TDS, mg/l	16	3494	0.5	24	1896	1.3	47	6890	0.7	187	4534	4.1
Conductivity, µmho/cm	14	2510	0.6	21	2395	0.9	42	6290	0.7	92	4435	2.1
Dissolved Oxygen, mg/l	0	< 0.1	0	0	< 0.1	0	0.02	< 0.1	20	0.01	< 0.1	10
Redox Potential, mv	0	-192	0	14	-200	7.1	12	-130	9.2	35	-143	24.5
pH	0.07	6.2	1.1	0.1	6.3	1.6	0	6.0	0	0	6.7	0
Acidity, mg/l	9.8	1454*	0.7	5.7	254	2.2	19.8	1336	1.5	19.8	374	5.3
Alkalinity, mg/l	1.3	14.3	9.1	1.4	12	11.7	3.5	34	10.3	1.4	81	1.7
Color, cpu	68	483	14.1	29.0	78	37.2	0.7	6	11.7	0	5	0
Turbidity, JTU	20.5	74.5	27.5	2.1	33.5	6.3	43.1	58.5	73.7	2.8	132	2.1
Organics												
TOC, mg/l	0	5.7	0	0.1	5.6	1.8	0.1	3.5	2.9	0.6	10.6*	5.7
Phenol, µg/l	0.78	1.8	43.3	0.20	< 1.0	20.0	0	1.9	0	--	< 1.0	--
THMFP, µg/l	--	23	--	0	< 5	0	0	< 5	0	0.92	<5	18.4

[1] σ = standard deviation
$\bar{X}$ = mean
% = precision ($\sigma/\bar{X}$ x 100)

* 7-day

TABLE 19

ANALYTICAL AND SAMPLING VARIANCE FOR METALS
(1- and 2-day samples for run 5)

Metal	Standard Deviation, σ	Mean, $\bar{X}$	Precision, %
Hg	0.0064	0.0225	28.4
Se	0.0107	0.179	6.0
Cd	0.0011	0.001	110
Zn	0.0023	0.0520	4.5
As	0.0640	0.235	27.2
Mn	0.0586	1.59	3.7
Cu	0.0064	0.0318	20.1
Al	0.0439	0.222	19.8
Fe (1 day)	0.104	0.577	18.0
Fe (2 day)	4.56	17.9	25.5
Pb	0.0250	0.279	9.0
Ni	0.0031	0.0531	5.8
Cr	0.00068	0.0169	4.0
Ba	0.0447	0.144	31.0

A problem was encountered with the color and turbidity tests. After filtering, the samples developed a precipitate. This precipitate could be filtered out but would reappear in a few minutes. The color measurement procedure was modified after run 3 to eliminate the interference. Turbidity measurements were made with the precipitate in the samples. The yellow-brown precipitate was postulated to be $Fe(OH)_3$ or Fe_2O_3. As the samples were handled, oxygen was dissolving into them causing the hydration of the iron. Consistent color and turbidity measurements were not possible since the samples were so unstable.

Redox potential measurements showed little variation during the testing except for the last two measurements in run 5. Phenol measurements had a high percent error but this was due to the accuracy of the test along with the very low values measured. The same was true for THMFP from run 5.

As can be seen from Table 19, several metals had high variability. The concentrations were low since the 1-day and 2-day samples were analyzed for variance, and the percent deviations were high as a result. Both Hg and Cd measurements were actually below the lower detectable limits. Both Mg and Ag were not measured for variance.

The percent solids for each run were determined by sampling on the tenth day of a run and weighing, drying and re-weighing triplicate sample portions. The average values are presented in Table 19. In run 4, the drum of coal obtained from Lakeland did not contain enough coal to mix a proper volume of a 50% slurry. Therefore, it was necessary to add more water to provide enough slurry to operate the pipeline and to obtain the proper amount of samples for analysis.

TABLE 20

PERCENT SOLIDS FOR EACH SLURRY RUN

Run No.	2	3	4	5
% Solids	53	47	34	48

Tables 20 and 21 show the average values for the water quality parameters of runs 2 and 3, respectively. These runs did not include the corrosion inhibitor. Tables 22 and 23 show the average values for runs 4 and 5, respectively, which included the corrosion inhibitor. A discussion of the parameters and their behavior is presented in the following pages.

Sulfates

Sulfate is an oxidized form of sulfur. The eastern coal used to make the slurries contained large amounts of sulfur, as shown in

TABLE 21

DATA SUMMARY TABLE FOR RUN 2

Parameter, Units	Typical Mix Water	Average Concentrations in Slurry Filtrate by Time after Start of Run						
		3-hours	7-hours	1-day	2-days	4-days	7-days	10-days
General								
Sulfates, mg/l	<2	1090	1297	1360	1371	1731	1683	1680
Chlorides, mg/l	19	24.1	27.0	38.6	47.3	61.7	74.3	78.1
TDS, mg/l	207	2016	1952	2194	2499	3235	3403	3494
Conductivity, μmho/cm	366	1720	1665	1810	1990	2420	2510	2510
Dissolved Oxygen, mg/l	7.9	4.7	0.5	0.4	0.3	<0.1	<0.1	<0.1
Redox Potential, mv	526	277	181	78	-48	-109	-179	-192
pH	7.0	3.5	4.4	4.9	5.7	5.8	6.1	6.2
Acidity, mg/l as $CaCO_3$	-96	910	805	845	890	1360	1450	1450
Alkalinity, mg/l as $CaCO_3$	120	(*)	(*)	(*)	23	13	17	14
Color, CPU	6	(12)	(12)	(39)	(133)	(118)	(212)	(483)
Turbidity, JTU	5.3	0.9	3.3	(15)	(27)	(32)	(34)	(74)
Organics								
TOC, ppm	14	5.5	3.9	4.8	5.5	6.0	6.1	5.7
THMFP, ppb	131.1	-	-	-	-	-	-	23
Phenols, ppb	-	-	<1.0	-	<1.0	-	1.1	1.8
Metals (mg/1)								
Hg*	0.076	0.382	0.324	0.424	0.475	0.740	0.762	0.801
Se*	0.242	0.283	0.317	0.265	0.321	0.466	0.576	0.534
Cd	0.006	0.063	0.046	0.031	0.041	0.066	0.077	0.084
Zn	0.071	2.29	1.73	0.816	0.281	0.239	0.250	0.238
As*	0.045	0.423	0.420	0.382	0.495	0.706	0.863	0.771
Mn	0.009	4.23	4.71	5.52	8.66	15.0	15.0	15.0
Cu	0.016	0.398	0.024	0.012	0.017	0.025	0.012	0.047
Al	0.033	21.2	5.55	1.35	0.475	0.901	0.516	0.780
Fe	1.28	114	174	300	368	524	520	529
Pb	0.029	0.444	0.446	0.450	0.388	0.503	0.521	0.569
Ni	0.002	1.57	1.26	0.497	0.113	0.111	0.120	0.225
Cr	0.004	0.056	0.050	0.055	0.030	0.045	0.042	0.060
Ba	0.015	0.166	0.121	0.067	0.150	0.171	0.135	0.120
Mg	11.0	80.4	80.4	82.4	83.2	89.6	90.0	91.2
Ag	0.002	0.037	0.029	0.028	0.038	0.038	0.039	0.038

NOTE: (*) = unfiltered sample
( ) = data not valid, precipitation occurs after filtration
* = data suspect - analytical problems

TABLE 22

DATA SUMMARY TABLE FOR RUN 3

Parameter, Units	Typical Mix Water	Average Concentrations in Slurry Filtrate by Time after Start of Run						
		3-hours	7-hours	1-day	2-days	3-days	6 -days	10-days
General								
Sulfates, mg/1	<2	795	735	790	770	950	930	1005
Chlorides, mg/1	19	48	59	77	96	109	141	154
TDS, mg/1	207	1207	1239	1286	1432	1566	1870	1896
Conductivity, µmho/cm	366	1246	1270	1369	1436	1528	1731	2395
Dissolved Oxygen, mg/1	7.9	0.30	0.11	<0.1	<0.1	<0.1	<0.1	<0.1
Redox Potential, mv	526	145	135	46	-15	-60	-125	-200
pH	7.0	4.9	5.2	5.4	5.8	6.0	6.2	6.2
Acidity, mg/1 as $CaCO_3$	-96	29.4	40.8	114.2	171.2	196.1	304.8	254.2
Alkalinity, mg/1 as $CaCO_3$	120	12.4	14.3	12.4	21.4	17.3	27.8	12.4
Color, CPU	6	4	3	2	56*	20*	53*	78*
Turbidity, JTU	5.3	6.8	18.5*	21.5*	77.5*	102.5*	96.5*	33.5*
Organics								
TOC, ppm	14	9.4	6.3	2.3	4.4	6.2	6.4	5.6
THMFP, ppb	131.1	-	-	-	-	-	-	<5
Phenols, ppb	-	-	-	-	-	<1.0	1.30	<1.0
Metals (mg/1)								
Hg*	0.076	<0.050	<0.050	<0.050	<0.050	0.055	0.081	0.087
Se*	0.242	0.112	0.134	0.159	0.131	0.194	0.179	0.200
Cd	0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Zn	0.071	0.290	0.203	0.113	0.113	0.134	0.104	0.066
As*	0.045	0.279	0.343	0.333	0.487	0.437	0.493	0.488
Mn	0.009	3.90	4.02	4.43	4.21	5.37	5.98	6.86
Cu	0.016	0.015	0.019	0.019	0.017	0.033	0.028	0.019
Al	0.033	0.158	0.225	0.219	0.128	0.151	0.234	0.162
Fe	1.28	2.25	10.9	-**	59.0	102	168	188
Pb	0.029	0.148	0.147	0.162	0.159	0.179	0.206	0.226
Ni	0.002	0.473	0.250	0.091	0.060	0.081	0.045	0.066
Cr	0.004	0.006	0.005	0.007	0.009	0.010	0.015	0.014
Ba	0.015	0.144	0.108	0.108	0.093	0.066	0.096	0.083
Mg	11.0	54.0	53.2	54.3	50.1	58.0	61.8	65.8
Ag	0.002	0.003	0.002	0.005	0.003	0.006	0.007	0.005

NOTE: * Precipitate formed, data not valid. Data suspect, analytical problems.
** Missing data.

TABLE 23

DATA SUMMARY TABLE FOR RUN 4

Parameter, Units	Typical Mix Water	Average Concentrations in Slurry Filtrate by Time after Start of Run						
		3-hours	7-hours	1-day	2-days	4-days	7-days	10-days
General								
Sulfates, mg/1	<2	2330	2330	2570	3150	4510	4100	3940
Chlorides, mg/1	19	66.3	80.8	106.0	134.0	135.0	150.0	175.0
TDS, mg/1	207	5096	4974	5053	5062	7117	7407	6890
Conductivity, µmho/cm	366	5530	5420	5565	6115	6565	6475	6290
Dissolved Oxygen, mg/1	7.9	0.81	0.37	0.20	<0.1	<0.1	<0.1	<0.1
Redox Potential, mv	526	175	90	-96	-68	-94	-120	-130
pH	7.0	5.8	6.5	6.5	5.9	5.8	5.9	6.0
Acidity, mg/1 as $CaCO_3$	-96	539	604	504	923	1470	1688	1336
Alkalinity, mg/1 as $CaCO_3$	120	276	188	46	24	21	20	34
Color, CPU	6	10	9	8	13	6	5	6
Turbidity, JTU	5.3	4.8	6.5	62.0*	44.0*	68.5*	44.0*	58.5*
Organics								
TOC, ppm	14	<2.0	3.1	4.3	4.1	4.4	4.6	3.5
THMFP, ppb	131.1	-	-	-	-	-	-	<5
Phenols, ppb	-	-	-	-	-	<1.0	1.9	1.0
Metals (mg/1)								
Hg*	0.076	0.0505	<0.050	0.0579	0.139	0.233	0.250	0.256
Se*	0.242	0.305	0.255	0.346	0.424	0.395	0.429	0.444
Cd	0.006	0.0103	0.0066	0.0079	0.0159	0.0122	0.0146	0.0151
Zn	0.071	0.172	0.128	0.107	0.240	0.234	0.286	0.222
As*	0.045	0.249	0.279	0.327	0.462	0.399	0.395	0.478
Mn	0.009	12.1	7.84	5.43	14.8	17.8	22.6	25.5
Cu	0.016	0.0195	0.0344	0.0214	0.0208	0.0208	0.0214	0.0230
Al	0.033	0.397	0.293	0.409	0.324	0.433	0.629	0.597
Fe	1.28	0.981	0.440	21.9	257	463	485	470
Pb	0.029	0.465	0.433	0.408	0.497	0.450	0.462	0.483
Ni	0.002	0.620	0.121	0.101	0.164	0.201	0.260	0.455
Cr	0.004	0.366	0.0428	0.0384	0.0571	0.0315	0.0356	0.0376
Ba	0.015	0.0445	0.0925	0.117	0.184	0.139	0.104	0.0081
Mg	11.0	268	151	155	173	193	200	198
Ag	0.002	0.0124	0.0097	0.0131	0.0165	0.0200	0.0234	0.0172

NOTE: *Precipitate formed, data not valid. Data suspect - analytical problem.

TABLE 24

DATA SUMMARY TABLE FOR RUN 5

Parameter, Units	Typical Mix Water	Average Concentrations in Slurry Filtrate by Time after Start of Run						
		3-hours	7-hours	1-day	2-days	4-days	7-days	10-days
General								
Sulfates, mg/l	<2	1400	1510	1340	2570	2340	2760	3420
Chlorides, mg/l	19	65.8	78.2	117	133	159	170	180
TDS, mg/l	207	3699	3580	3332	3667	4130	4432	4534
Conductivity, µmho/cm	366	3730	3540	3345	3810	4325	4345	4435
Dissolved Oxygen, mg/l	7.9	0.30	0.33	<0.10	<0.10	<0.10	<0.10	<0.10
Redox Potential, mv	526	108	35	-140	-135	-193	-154	-143
pH	7.0	6.4	6.7	7.2	6.7	6.7	6.6	6.7
Acidity, mg/l as $CaCO_3$	-96	264	228	143	213	371	331	374
Alkalinity, mg/l as $CaCO_3$	120	239	227	269	131	59	89	81
Color, CPU	6	7	10	8	2	11	11	5
Turbidity, JTU	5.3	1.0	1.1	1.8	57*	161*	144*	132*
Organics								
TOC, ppm	14	2.0	4.5	21.0	6.0	10.2	10.6	33.8
THMFP, ppb	131.1	-	-	-	-	-	-	<5
Phenols, ppb	-	-	-	-	-	<1.0	<1.0	<1.0
Metals (mg/l)								
Hg*	0.076	<0.050	<0.050	<0.050	<0.050	<0.050	0.0582	0.0521
Se*	0.242	0.168	0.207	0.183	0.190	0.225	0.229	0.167
Cd	0.006	<0.005	<0.005	<0.005	<0.005	<0.005	0.005	0.005
Zn	0.071	0.0100	0.0771	0.0371	0.0795	0.0670	0.0295	0.0735
As*	0.045	0.208	0.197	0.133	0.259	0.320	0.403	0.274
Mn	0.009	2.99	1.77	0.789	2.80	6.06	6.80	7.60
Cu	0.016	0.0041	0.0282	0.0360	0.0364	0.0174	0.116	0.0124
Al	0.033	0.173	0.289	0.233	0.255	0.247	0.285	0.291
Fe	1.28	0.0554	0.462	0.624	16.4	55.4	54.8	69.3
Pb	0.029	0.252	0.243	0.211	0.278	0.326	0.334	0.358
Ni	0.002	0.0994	0.0476	0.0252	0.0795	0.138	0.169	0.180
Cr	0.004	0.0147	0.0163	0.0137	0.0196	0.0202	0.0242	0.0192
Ba	0.015	0.0740	0.0866	0.0422	0.182	0.161	0.0837	0.0637
Mg	11.0	82.0	64.5	51.6	81.5	121	124	128
Ag	0.002	0.0052	0.0042	0.0021	0.0054	0.0114	0.0137	0.0140

NOTE: * Precipitate formed, data not valid. Data suspect - analytical problem.

Table 12. A small fraction of this sulfur leached into the carrier water during the slurry pipelining. This is evidenced by comparing the tap water blank and the slurry filtrate sulfate concentrations. The increase in sulfate concentrations with time is shown in Figure 3. The concentrations generally increased and leveled off, indicating that equilibrium conditions had been approached. This leveling off may also have been caused by the lack of free oxygen in the pipeline, which would limit the oxidation of sulfur into sulfate.

Run 2 exhibited higher sulfate concentrations than run 3 (see Figure 3). This was probably due to the higher percent sulfur in the solid coal for run 2 (see Table 12). Similarly, run 4 filtrate contained more sulfate than run 5 and the solid coal for run 4 contained more sulfur.

The addition of the corrosion inhibitor appeared to increase the sulfate concentrations substantially. The inhibitor did not contain sulfur or sulfur compounds. Therefore, some ion exchange between the chemical additives and the sulfate compounds in the slurries most likely occurred. This could have made some sulfates more soluble and resulted in higher concentrations in the slurry filtrate.

Chlorides

Chlorides are found in most coals. The chloride concentrations in the slurries were much higher than the tap water concentration indicating that chlorides leached from the coal into the

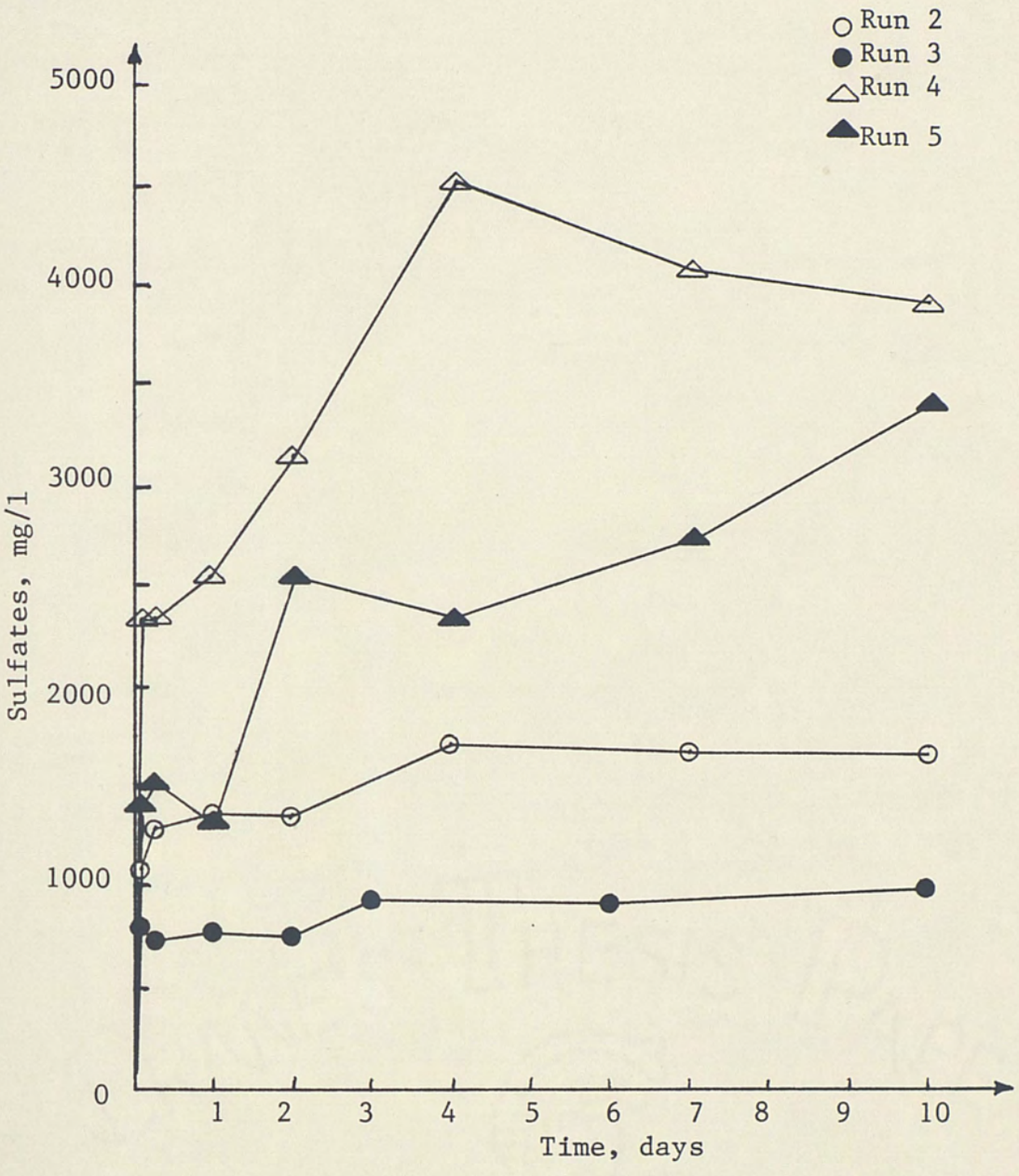

Fig. 3. Variation of sulfates in coal slurry filtrate with pipeline detention time.

slurry water. Chlorides concentrations for runs 4 and 5 were very similar. Run 3 had slightly less chlorides than runs 4 and 5, and run 2 had roughly half the chlorides of run 3. The chloride concentration of the solid coal was not tested, so no explanation for run 2 is available. In all cases, the concentrations increased and leveled off with time, as shown in Figure 4.

TDS

Total dissolved solids is that which passes through a 0.45 micron filter and remains after the sample is evaporated to dryness. Major constituents include sulfates, sodium, chlorides, calcium, magnesium and iron.

TDS in the slurries increased immediately from the tap water values and then leveled off. Figure 5 represents the TDS concentrations versus time for each slurry run. As shown, TDS levels in run 2 were much higher than in run 3. Sulfates and magnesium were both higher in run 2, although chlorides were less. Sodium and calcium concentrations are unknown but may have contributed to the difference.

It appears that the corrosion inhibitor contributed significantly to the dissolved solids because both runs 4 and 5 had more TDS than runs 2 or 3. Run 4 exhibited more TDS than run 5 and this agrees with the higher levels of sulfates and magnesium in run 4.

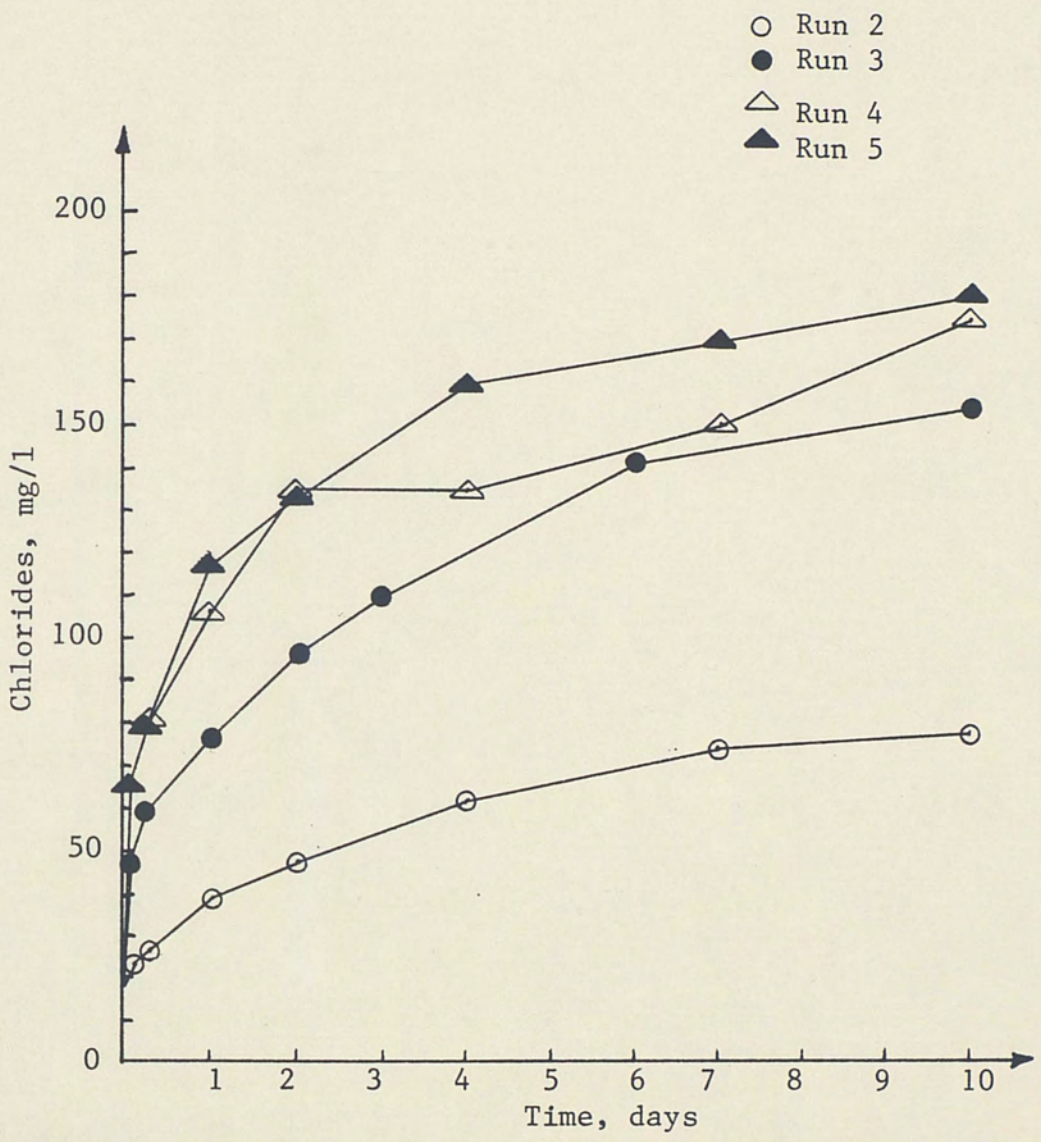

Fig. 4. Variation of chlorides in coal slurry filtrate with pipeline detention time.

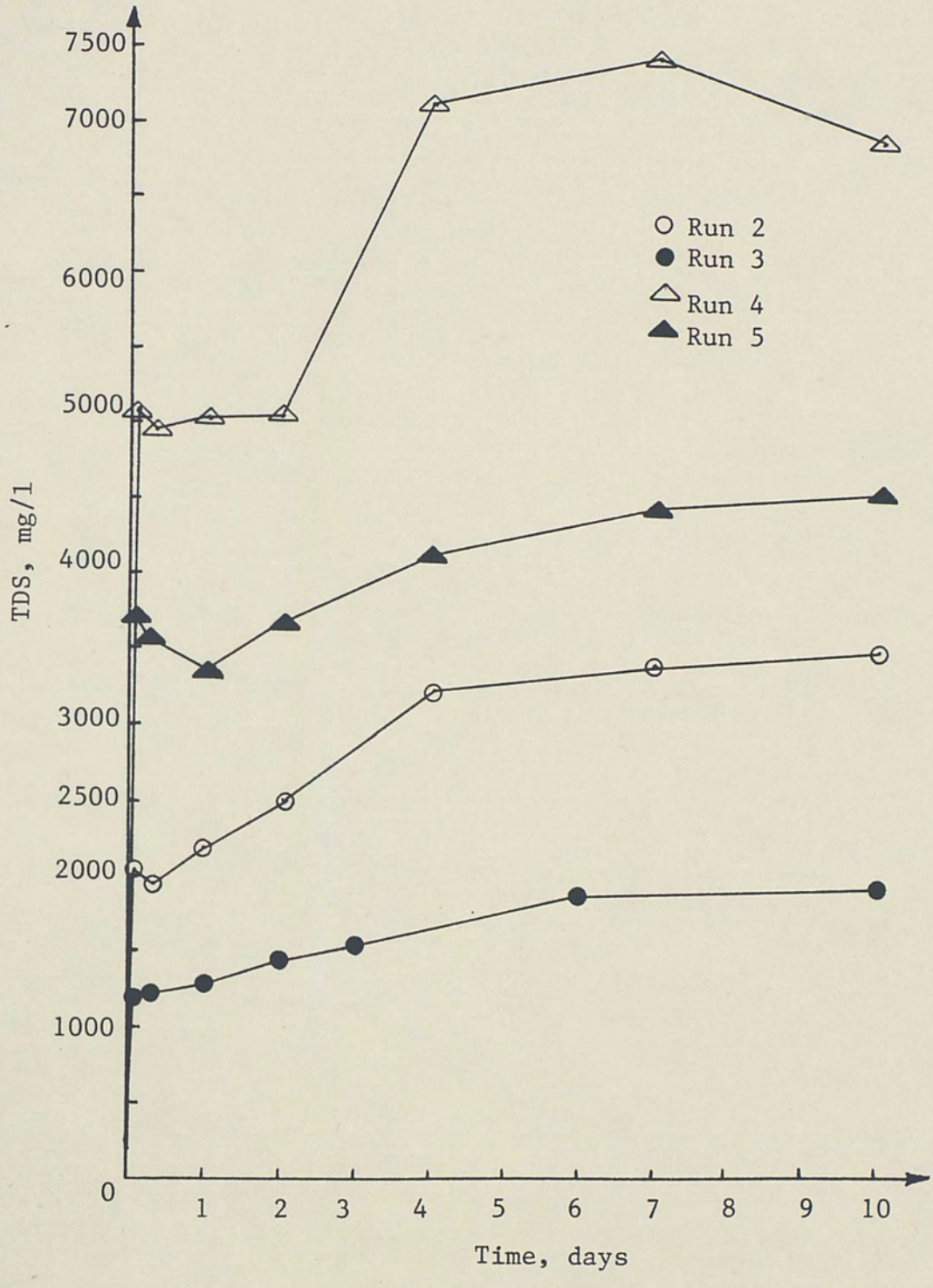

Fig. 5. Variation of TDS in coal slurry filtrate with pipeline detention time.

Conductivity

The electrical conductivity of water is a function of its ionic strength. Therefore, it is an indirect measure of the total dissolved solids present. The conductivity of the slurries followed the same pattern as the total dissolved solids. The levels initially increased significantly and then gradually increased at a rate slightly less than the TDS rate of increase. Similar comparisons between slurry runs can be made for conductivity as were made for TDS.

Dissolved Oxygen

Dissolved oxygen present in the slurry could have originated from oxygen trapped in the pulverized coal, from oxygenation as the slurry was mixed, from leakage into the reactor during the pipeline operation, or from oxygenation during sampling and handling of the samples during DO measurements. Any leakage into the system or oxygenation during sampling and handling was very slight since precautions were taken to avoid this. The pipeline and reactor were well sealed and nitrogen blanketed the slurry in the reactor tank. Samples were collected in properly capped bottles and the DO measurements were made immediately.

Dissolved oxygen in the tap water was measured to be 7.9 mg/l (Table 16). During the mixing of the slurry for run 3, a DO sample was collected from the mixing drum and the DO was found to be 5.4 mg/l. The DO continued to decrease with time for several hours.

Apparently, the oxygen was being consumed by coal-water chemical reactions.

The DO levels in all slurry runs dropped immediately to less than 1 mg/l in the pipeline. After 1-2 days, the DO level was below the detectable limit of 0.1 mg/l.

Redox Potential

Oxidation-reduction or "redox" reactions largely influence the behavior of compounds containing carbon, nitrogen, sulfur, iron and manganese. The platinum redox probe used to measure the coal slurries contained a reference solution and a pH meter was used to measure the voltage difference. A positive reading indicates free electrons which will allow a reduction reaction. Oxygen is an oxidizing agent and will be involved in oxidation reactions producing a positive redox potential. As seen in Tables 21-24, the redox potential dropped to a negative value as the DO level approached zero.

Figure 6 shows the redox potential behavior with time for all coal slurry runs. Runs 2 and 3 decreased rapidly and slowly leveled off. Runs 4 and 5 dropped abruptly and remained relatively stable after 1 day.

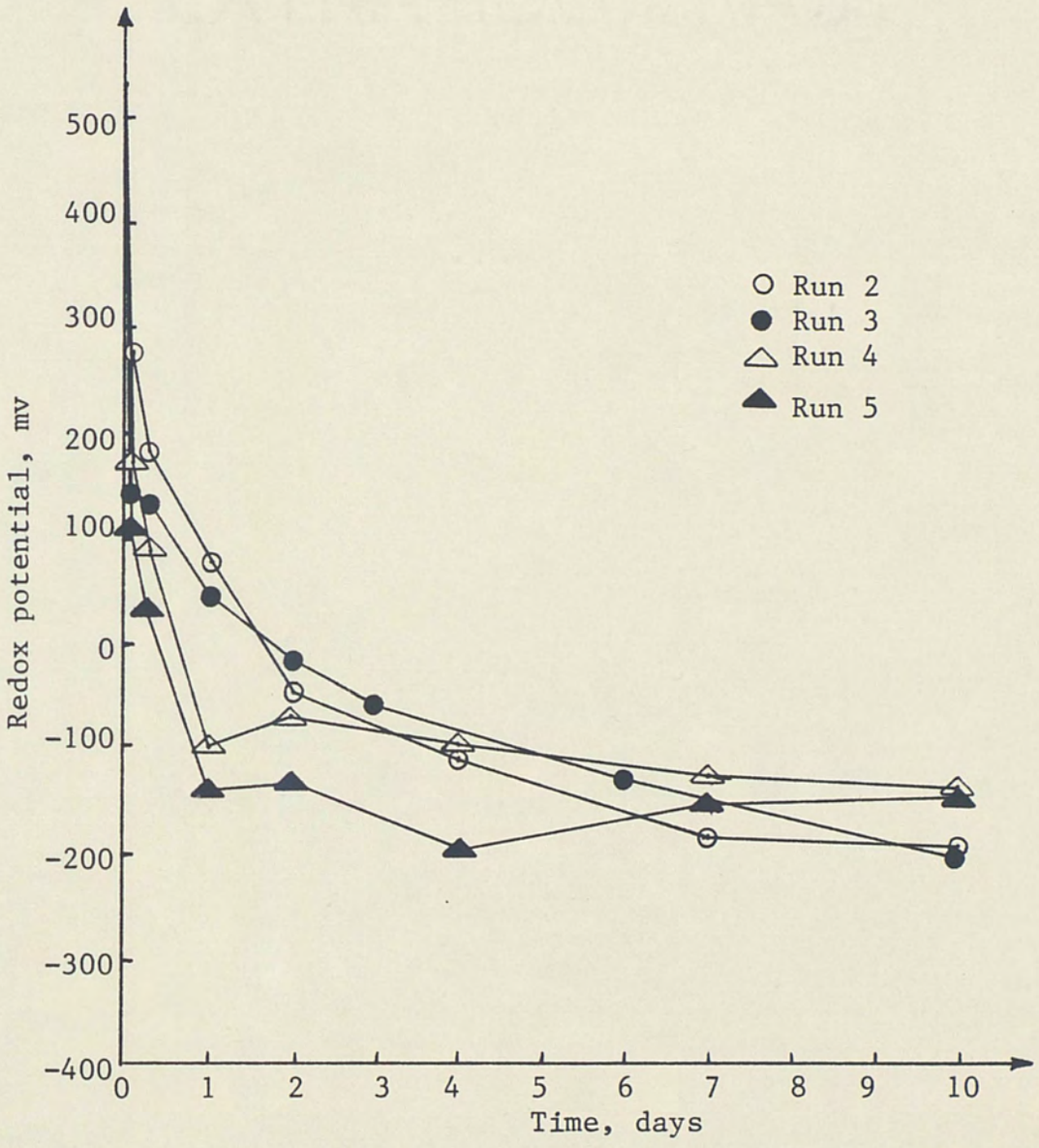

Fig. 6. Variation of redox potential in coal slurry filtrate with pipeline detention time.

pH

The solubility of many metals is very pH dependent. Acidic conditions generally result in solubilization of metals and high pH generally results in the precipitation of metals as metallic hydroxides.

Changes in pH occur as the result of reactions that release hydrogen, H^+, or hydroxyl, OH^-, ions. In a coal slurry, a reaction involving sulfur, water and oxygen can produce sulfuric acid which will lower the pH. This apparently occurred in the coal slurries tested here. As shown in Figure 7, the pH dropped initially and then climbed steadily in runs 2 and 3. Sulfate concentrations in run 2 were higher than in run 3, thereby producing a lower pH as more H_2SO_4 was formed. The pH climbed after the initial drop possibly due to the lack of oxygen, which would limit H_2SO_4 formation, and the subsequent neutralization of the acid.

Runs 4 and 5 remained stable, with respect to pH. The corrosion inhibitor apparently added alkalinity (borates) which buffered any addition of acids. The pH of run 4 was less than that of run 5 which coincides with the higher sulfate concentration of run 4.

Acidity

Acidity is a measure of the capacity of a water to neutralize strong bases. This capacity is attributable to strong and weak

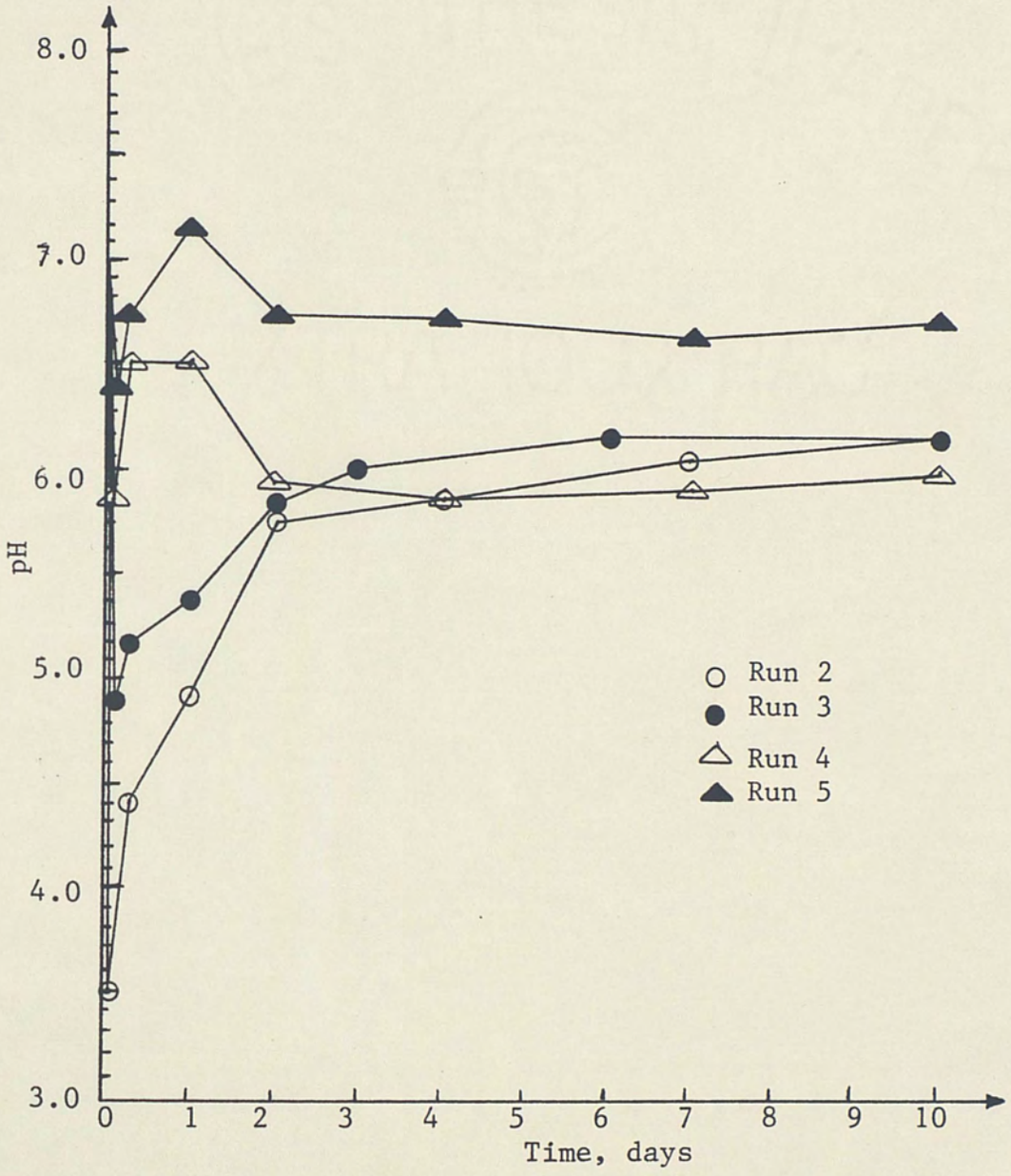

Fig. 7. Variation of pH in coal slurry filtrate with pipeline detention time.

acids in the water. For these coal slurry tests, the acidity was equivalent to the amount of strong base which must be added per liter to raise the pH to an endpoint of 8.3.

As seen from Figure 8, the acidity climbed and leveled off after 7 days for all slurries. The higher values for run 2 over run 3 were probably attributable to the more acidic conditions of run 2. Run 4 had much higher acidity values than run 5 which was partly due to the more acidic conditions in run 4.

For an unknown reason, a drastic change occurred in the 1-day samples for run 5. The data for the 1-day sample did not fit the trends for several parameters. Sulfates dropped almost 200 mg/l instead of increasing. This coincided with a drop in TDS and conductivity. The pH rose from 6.7 to 7.2, after which it returned to 6.7 for the 2-day sample. Acidity decreased as 85 mg/l instead of increasing and alkalinity increased unexpectedly by 40 mg/l. TOC jumped abruptly and several metal concentrations decreased, due to the rise in pH. All of the parameters are interrelated and a change in one parameter could have affected the others. The parameter which was initially affected is unknown, but may have been either sulfates, acidity or alkalinity.

Alkalinity

Alkalinity is a measure of the capacity of a water to neutralize strong acids. The principal components of alkalinity are bicarbonate

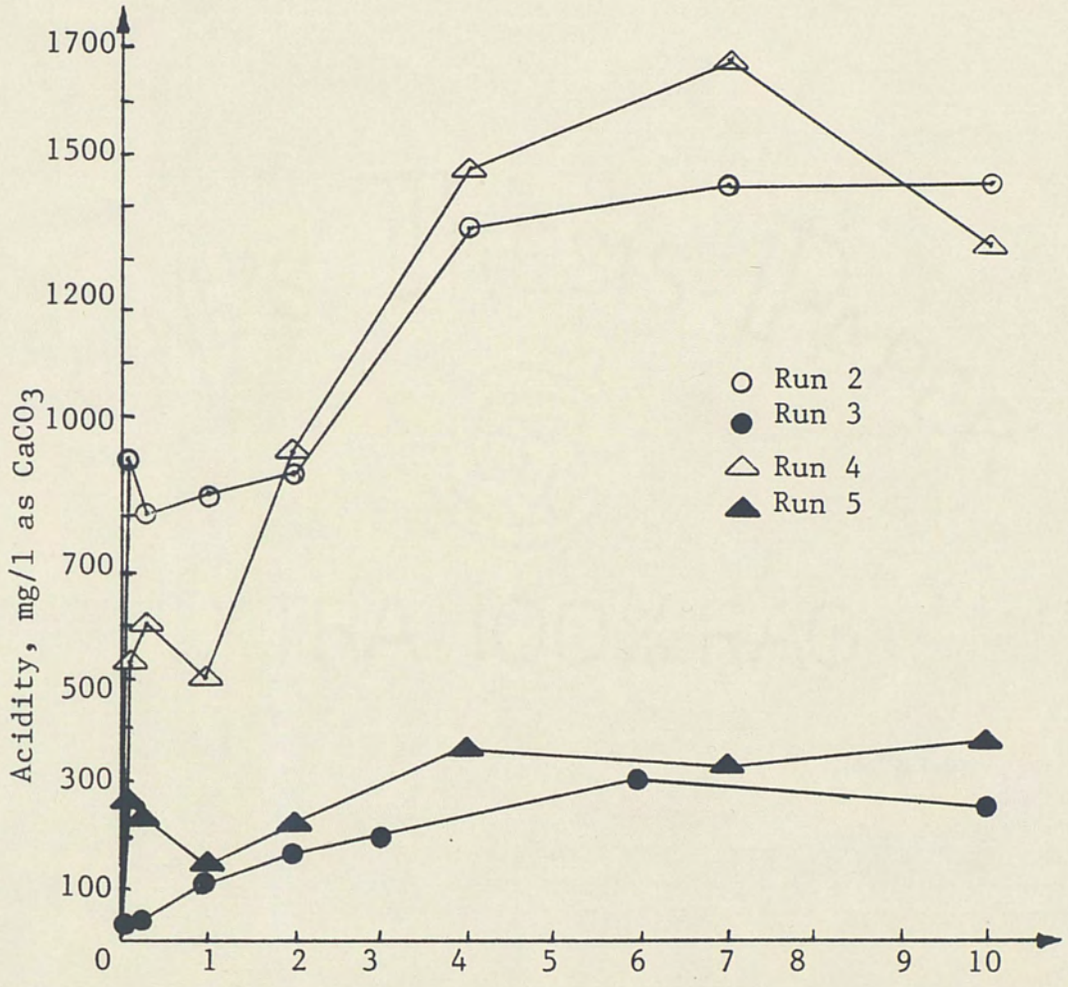

Fig. 8. Variation of acidity in coal slurry filtrate with pipeline detention time.

(HCO_3^-), carbonate ($CO_3^=$), and hydroxyl (OH^-) ions as well as salts of borate, phosphate, silicate, ammonia and organic bases. In these slurry tests, the alkalinity was defined as the amount of strong acid which must be added per liter to lower the pH to an endpoint of 3.7.

From Figure 9, it is seen that in runs 2 and 3 the alkalinity remained fairly stable, in the range of 12-17 mg/l as $CaCO_3$, with a few outlying data points. These low alkalinity values show that most of the buffering capacity of the slurry was consumed immediately by sulfuric acid or acidic material, since the tap water alkalinity was relatively high at 120 mg/l as $CaCO_3$. No increase occurred with time indicating the absence of leaching of large amounts of alkaline substances from the coal.

Runs 4 and 5 behaved differently because of the additional alkalinity contained in the corrosion inhibitor. The alkaline-based inhibitor caused the values to be high initially and then the alkalinity decreased and leveled off. This high initial alkalinity prevented the pH from dropping when sulfuric acid was formed. Run 5 contained more alkalinity than run 4 and, as a result, the pH remained higher in run 5. The decrease in alkalinity with time could have been because of adsorption of the corrosion inhibitor to the coal particles or the walls of the pipeline.

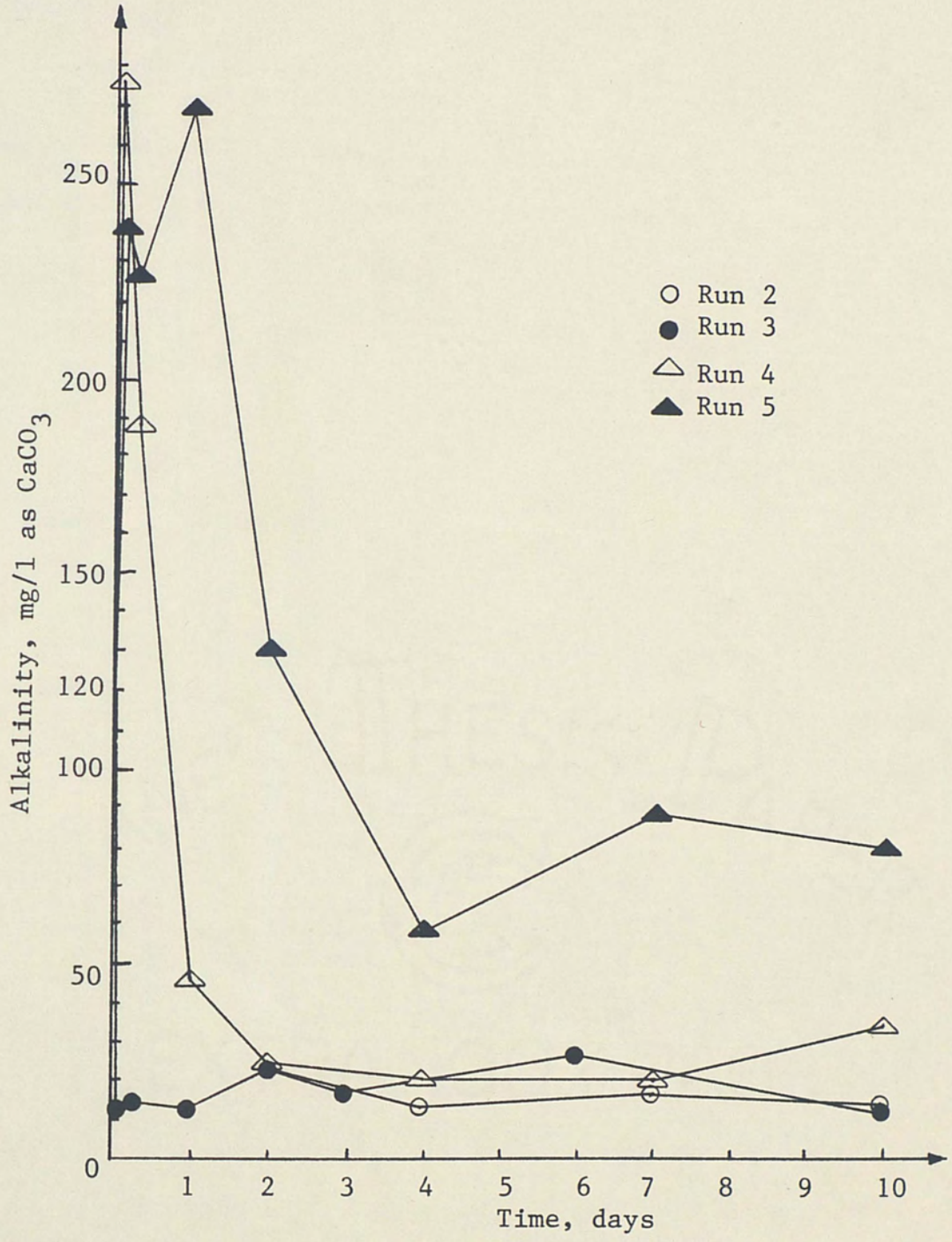

Fig. 9. Variation of alkalinity in coal slurry filtrate with pipeline detention time.

Color

The color of water is expressed quantitatively by measuring its absorbance at a set wavelength. Color in waters may be caused by humic substances or certain heavy metals. Primary color-causing substances in coal slurries are organics and manganese. Measurements of the true color must be done with caution. Precipitates or other solids in the sample may cause an apparent color. This apparent color should be filtered out to measure true color.

In the slurry measurements for color, apparent color became a problem. The filtrate was "crystal clear" immediately after filtering, but within a few seconds, a precipitate would form. The amount of precipitate, believed to be $Fe(OH_3)$, depended upon the amount of dissolved metals in the slurry. Color measurements of 20 cpu and above in Tables 21 and 22 were of samples containing precipitate and these values are not representative. The color measurement procedure was modified to eliminate the interference in runs 4 and 5. The pH was adjusted to 3 and then the samples were filtered through a 0.45 micron filter. The precipitate did not form at the low pH conditions.

As seen in Tables 21-24, the valid color measurements were all low with no apparent patterns occurring. Most values were less than 10 cpu. These low values occurred as a result of the low level of organics in the slurries. The manganese present must have been in an oxidized or complexed form since no manganese color was

evident. No increase in color occurred over the initial tap water value of 6 cpu.

Turbidity

Turbidity in water results from suspended matter which scatters light. The turbidity of coal slurries can be measured after the coal is removed to provide an idea of the separation efficiency.

Turbidity in the slurries was essentially zero after filtering, however, a precipitate formed as oxygen entered the samples, which caused turbidity. From Tables 21-24, it is seen that the samples taken within the first 24 hours, before significant metals concentrations developed, showed low turbidity values. As iron increased in the slurries, so did the turbidity due to $Fe(OH_3)$ formation. It is interesting to note that higher turbidity values occurred in the slurries with the higher pH values. Higher pH, of course, lowers the solubility of metals.

TOC

Total organic carbon levels in the slurry were found by measuring the total carbon levels and subtracting out the inorganic fractions. Since the samples were filtered, only the dissolved organic carbon was measured.

Organic materials in coals may be leached into the transport water of slurries, thereby producing high TOC values. This did not

occur in the slurries tested here. TOC levels dropped initially from the tap water value of 14 mg/l and then began to increase slightly. As seen in Figure 10, runs 2 and 3 continued to drop after initial mixing and climbed after 1 day. Runs 4 and 5 dropped to very low values initially and then climbed steadily. Perhaps the organics in the tap water were initially adsorbed onto the coal and then were slowly released. It is believed that higher pH will allow higher dissolved organic carbon concentrations. This can be seen when comparing runs 4 and 5. The jump in TOC at 1 day in run 5 was accompanied by a jump in pH. The large jump in the 10-day sample cannot be explained. Analytical error is a possibility.

THMFP

Trihalomethane formation potential is closely related to the organics in a water. As a water is chlorinated, and humic substances are present, a potential for the formation of haloforms exists. The amount of haloforms formed depends upon the amount of organics present, the amount of chlorine added, pH conditions and possibly several as yet unknown factors. THMFP research is relatively new.

Natural waters have a chlorine demand which is primarily influenced by organics, metals of iron and manganese, ammonia, sunlight, nitrites, and sulfur (18). It would seem that coal slurry filtrates would have a large chlorine demand. However, in prior tests of a coal slurry similar to the ones tested in runs 2-5, the demand was

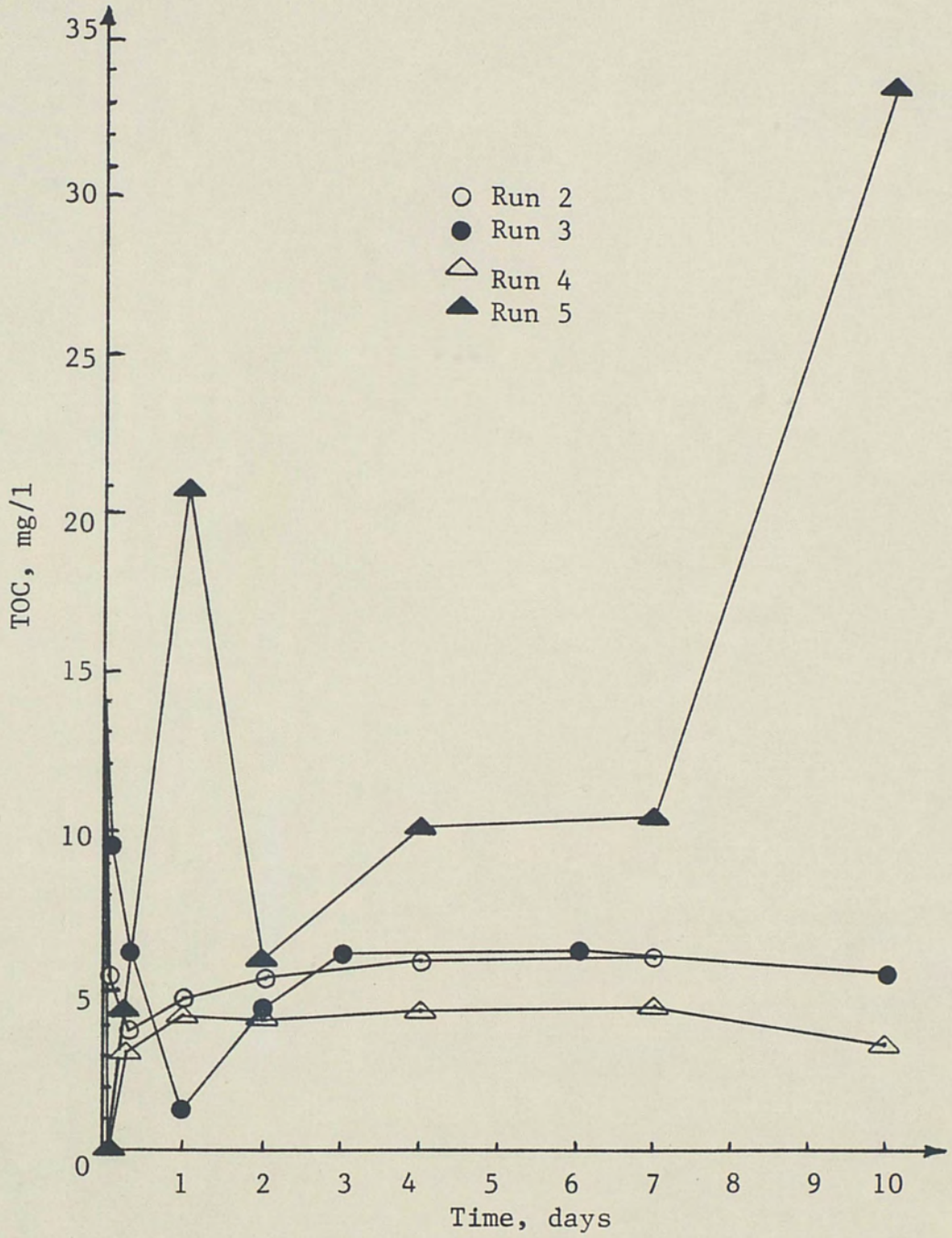

Fig. 10. Variation of TOC in coal slurry filtrate with pipeline detention time.

not large. A chlorine dose of 30 mg/l produced a chlorine residual of 24 mg/l, 40 mg/l produced a 36 mg/l residual, and higher doses produced residuals of approximately 80% of the dose. A chlorine dose of 5 mg/l was chosen for the THMFP testing, which is comparable to dosages used in practice for disinfection of wastewaters. It is seen now, from the low concentrations of THM's observed, that a larger chlorine dose could have been applied to the slurries to perhaps more accurately observe the THM formation potential.

The large concentrations of iron and manganese in the 10-day samples caused a chlorine demand much higher than expected. This demand was unpredictable and differed for each run. THMFP is a strong function of the available chlorine. A chlorine dose should be applied which will provide a residual after the incubation period to ensure a constant supply of chlorine for THM's to form. Therefore, a 48-hour chlorine residual test would have to be performed for each run to determine the optimum chlorine dose. For instance, the dose for run 4 would have to be much higher than that for run 5. Based on these complications, it is seen that the THMFP test may not be a valid test for coal slurry filtrates.

It is known that THM's form better at high pH conditions. Therefore, the coal slurry samples were raised to pH 8 before chlorination. The slurry samples were incubated for 48 hours in total darkness to exclude the effects of sunlight.

THMFP levels in the tap water were very high at 131 ppb. This was probably due to the lower expected chlorine demand and the higher TOC present in the tap water when compared with the slurries. The field blank samples contained more TOC than the tap water, but the chlorine demand was higher due to the iron present and THMFP was at 53.9 ppb. Only the 10-day samples of the slurries were analyzed. THMFP levels in the coal slurries were very low. All measured less than the lower detectable limit except for run 2, which measured 23 ppb. These low values probably occurred as a result of the low TOC levels and the high amounts of iron, manganese, sulfur and other chlorine demanding substances which did not allow trihalomethanes to form.

Samples for each slurry were treated with lime and alum to observe the treatability of coal slurry filtrates. THMFP was measured on these samples and higher values were observed in some cases where chlorine residuals probably existed after the 48-hour incubation period. Values ranged from 15 ppb for alum-treated to 35 ppb for lime-treated samples. Note that these values are still extremely low. The lower chlorine demand was probably due to the precipitation of iron and manganese during treatment. TOC values in these samples were lower than untreated samples.

After the project was completed, it was desired to determine the actual chlorine demand for the coal slurries that were tested. Spare samples were found from runs 4 and 5 which had been acidified

to pH 2 for metals analysis. Bacterial degradation of organics was not likely. The required dose of chlorine to produce a 48-hour residual was 400 mg/l and 5 mg/l for runs 4 and 5, respectively. These samples were then analyzed for THMFP and the results were 135 ppb and 10 ppb for runs 4 and 5, respectively. A chlorine dose of 400 mg/l is very impractical, however. In an effort to lower the chlorine demand of run 4, a portion of the sample was treated with lime to raise the pH to 11, and precipitate chlorine-demanding metals. A 48-hour residual was found for a dose of 5 mg/l and the resulting THMFP was 10 ppb. Because the THM levels are low, it suggests that THM formation potential in this particular coal slurry is small.

Phenols

Organics extracted from coal into transport waters may contain phenolic groups. The phenol content of the slurries was less than 2 ppb in all cases. Except for run 2, only the last three sample times were analyzed for phenols because of the length and difficulty of the test and because the early tests suggested that phenols were not present in the slurry. No phenols were detected in run 5. Since the solid coals were not analyzed for organic groups, the reasons are unknown for the phenol levels in each slurry.

Metals

Coals contain many metals which can be leached into slurry transport water. Low pH conditions will increase the solubilities of most metals.

The metal samples were filtered within one hour of sampling and then were treated with nitric acid to lower the pH to 2 or less. No precipitation of metals was allowed to occur. Samples were oxidized during handling, but the pH was adjusted to 2 before precipitation could result. Therefore, all dissolved metals were measured.

The concentrations of all metals in the slurries were observed to be higher than the tap water concentrations, indicating that metals definitely were leached from the coal. Variation in the dynamic behavior of individual metals was observed.

It has been stated previously that analysis of Hg, As and Se were in doubt because of lack of accuracy in measuring quality assurance samples. Although the exact concentrations of these metals is probably not accurate, it can be seen from Tables 21-24 that the concentrations steadily increased with time.

Cadmium was below the lower detectable limit in runs 3 and 5. In runs 2 and 4, cadmium concentrations rose initially then dropped after 7 hours and began to climb steadily.

Zinc decreased with time in runs 2 and 3, but increased in runs 4 and 5. Therefore, the corrosion inhibitor had an effect on the

slurry which allowed more zinc to become soluble. Zinc behavior with time is shown in Figure 11.

Manganese, iron and magnesium increased markedly in all slurries and continued to increase with time. A sudden jump in iron and manganese concentrations occurred at the 2-day samples for runs 4 and 5. Changes in other parameters which occurred at this time were a jump in sulfates, the DO went to zero, the redox potential turned negative, and the pH suddenly dropped slightly. A possible explanation is that the corrosion inhibitor coated the coal particles and kept the metals contained for the first day and then released them thereafter. Manganese and magnesium decreased initially in runs 4 and 5 and then began to increase after 2 days. Manganese and iron are plotted in Figures 12 and 13, respectively.

Copper, chromium and silver remained relatively stable throughout all runs. Concentrations of these metals were higher in run 2 than in run 3, as was the case with all metals. Lower initial pH conditions in run 2 may have solubilized more metals.

Aluminum rose quickly in run 2 to 21 mg/l and then decreased quickly. Aluminum in run 3 began at low levels and remained stable. Runs 4 and 5 showed a small increase in aluminum concentrations with time.

Lead increased slightly in runs 2 and 3. In runs 4 and 5, lead concentrations showed a slight decrease after the initial rise and then began to climb again after 2 days. Therefore, lead was affected in the same way as manganese and magnesium by the corrosion inhibitor.

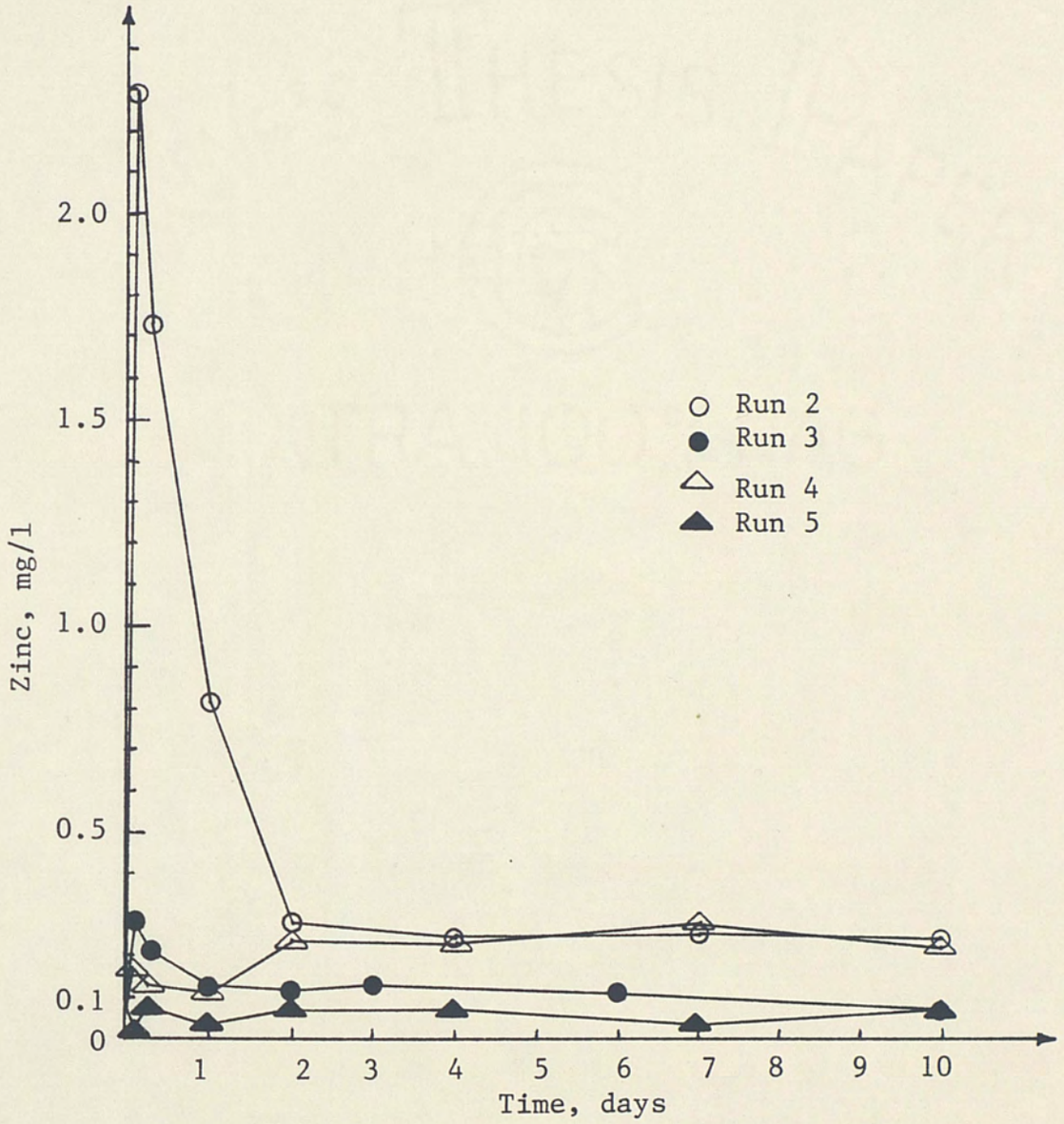

Fig. 11. Variation of zinc in coal slurry filtrate with pipeline detention time.

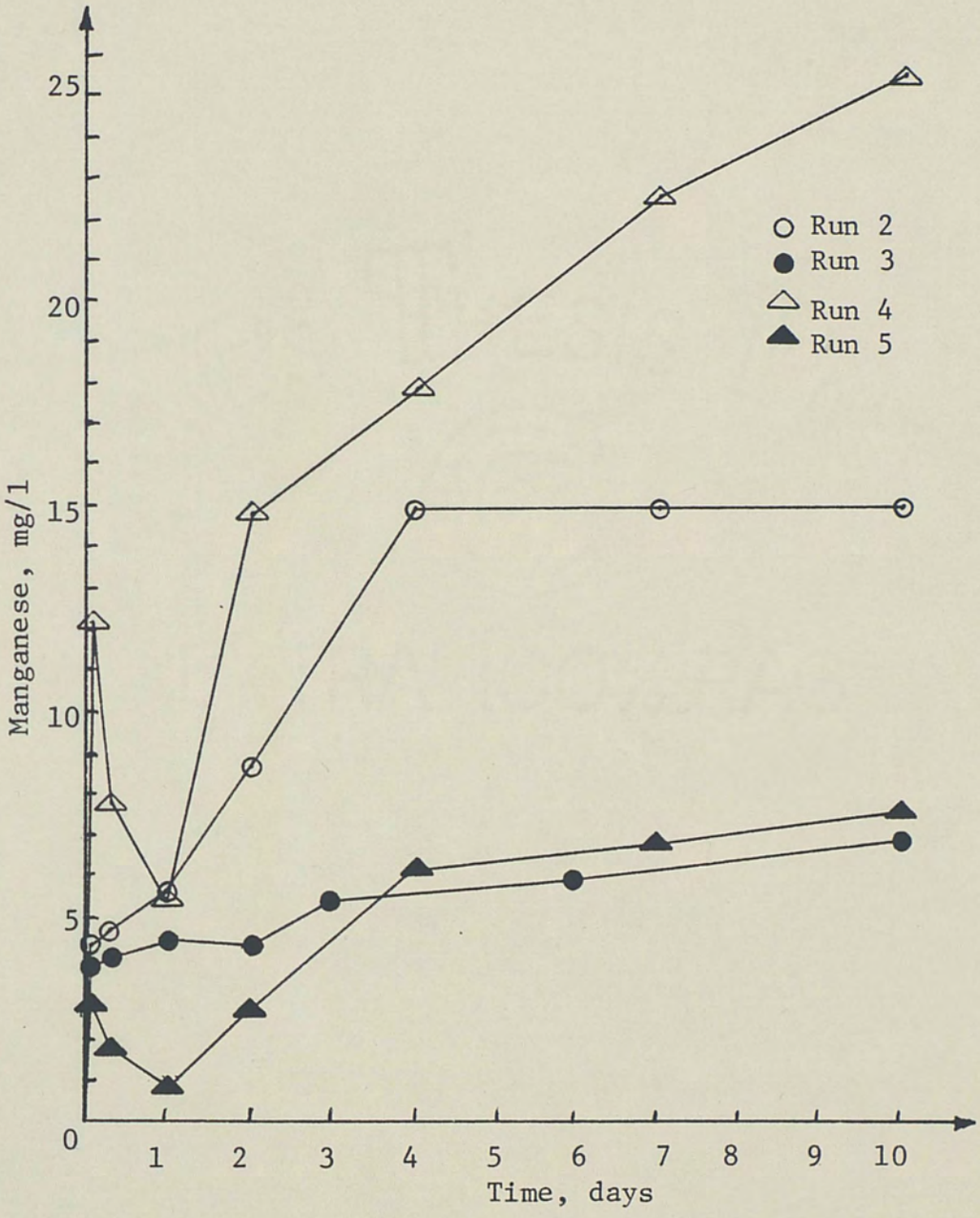

Fig. 12. Variation of manganese in coal slurry filtrate with pipeline detention time.

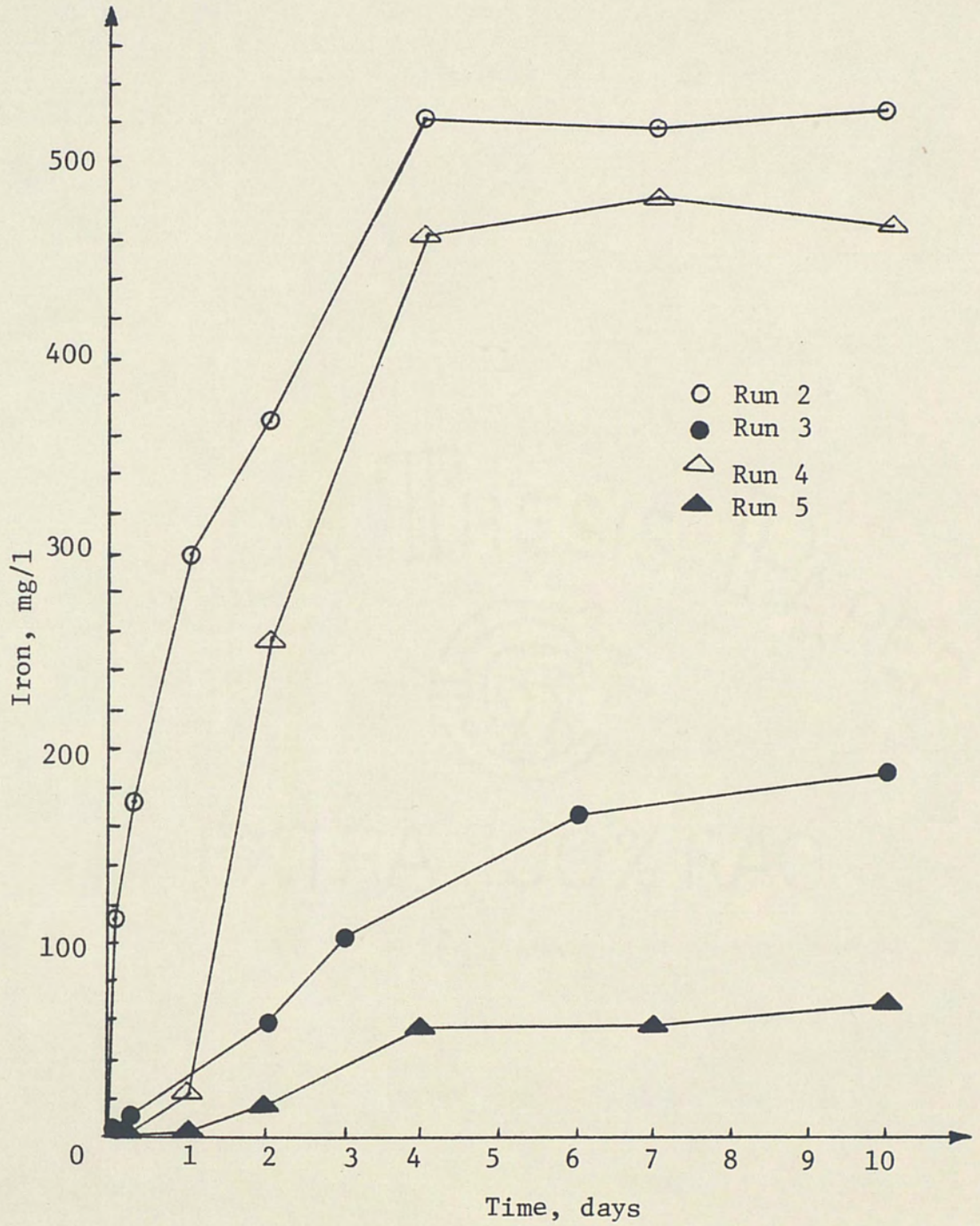

Fig. 13. Variation of iron in coal slurry filtrate with pipeline detention time.

Concentrations of nickel were shown to decrease after the initial rise in concentration and then increase after 2 days in runs 2 and 3. In runs 4 and 5, the increase occurred after 1 day. Nickel is shown in Figure 14.

Barium in runs 2 and 3 showed a slight decrease, but remained relatively stable and fluctuated up and down. Barium in runs 4 and 5 increased to a peak at 2-4 days and then began to decline. Figure 15 shows barium behavior with time for each slurry.

Summary

As can be seen in runs 2-5, the water quality characteristics of the coal slurries were different between each run. This was probably attributable to differences in the dry coal used to make up the slurries. This coal came from the same source which indicates that it is difficult to obtain a constant supply of coal with the same characteristics. It was shown that only slight variations in sulfur content of the coal can substantially affect the slurry water quality. It is expected, then, that the water quality characteristics of actual full-scale slurry pipelines will vary according to the input coal variation.

Based on the results obtained from the UCF studies, the slurry filtrate would require treatment before discharge. High concentrations existed for Hg, Fe, Mn, Mg, Se, Pb, Ag, Cd, sulfates, TDS and conductivity. Organics were not a problem. The filtrate would require aeration to raise the dissolved oxygen level. Treatment

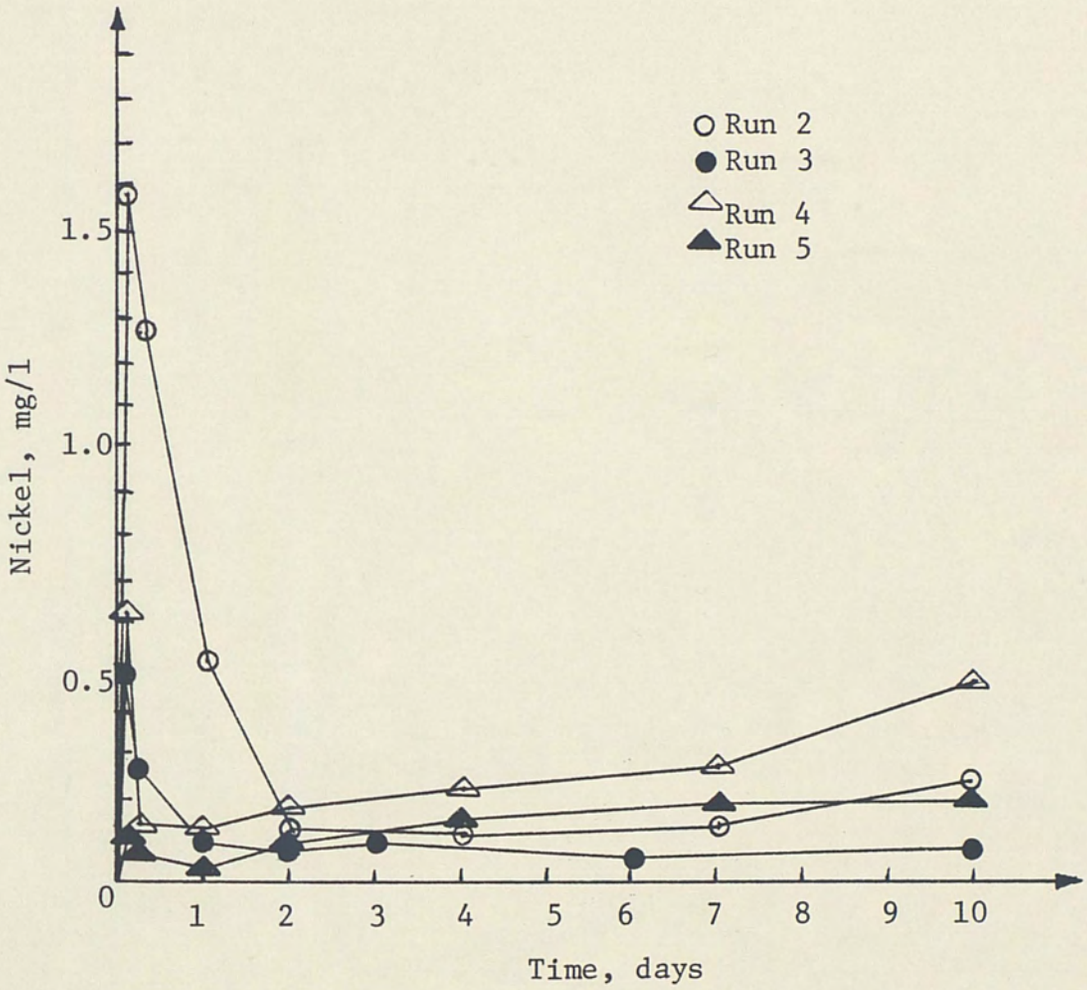

Fig. 14. Variation of nickel in coal slurry filtrate with pipeline detention time.

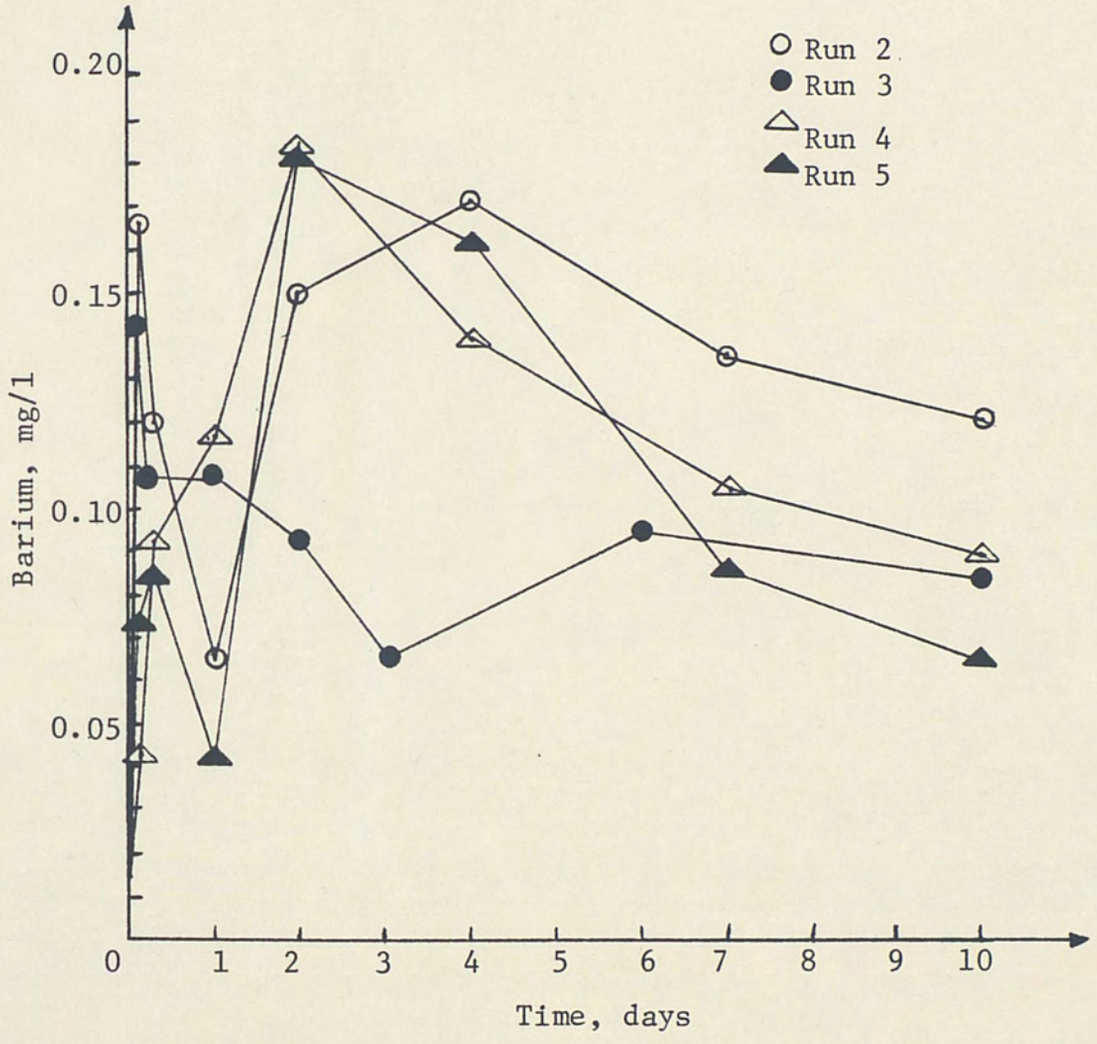

Fig. 15. Variation of barium in coal slurry filtrate with pipeline detention time.

with lime to raise the pH might be used to precipitate the heavy metals. Sulfate removal may be necessary. The TDS and conductivity would probably drop after any treatment that lowered the other parameters. The treatability of coal slurry filtrates will be discussed by Mr. Mark Flint in a future thesis at UCF.

Table 25 is a comparison between selected water quality parameters of western coal slurries and the eastern coal slurry tested here. Comparisons were made only between studies which were conducted similarly to the UCF studies. The runs which included a corrosion inhibitor were not compared.

It can be seen from Table 25 that the eastern coal slurries differed substantially from the western coal slurries. Values in Table 9 for Illinois and Kansas coal agree closely with the values for the Kentucky coal tested at UCF. Sulfates are generally higher in eastern slurries than in western slurries. The pH is slightly higher in western slurries. Alkalinity levels are lower for eastern coal when compared to western coal. The TOC was observed to be lower for eastern coal slurries, although the results of one study cannot be taken as absolute. Levels of iron and lead were higher in eastern slurries while levels of magnesium were lower for the eastern slurries. Heavy metals will be mostly influenced by concentrations in the particular coal and by pH conditions in the slurries.

TABLE 25

COMPARISON OF EASTERN AND WESTERN
COAL SLURRIES FOR SELECTED PARAMETERS

Parameter, Units	Eastern Slurry*	Western Slurry**
Sulfate, mg/l	1000 - 1700	400 - 1000
pH, units	6.2	6.0 - 7.8
Alkalinity, mg/l as $CaCO_3$	12 - 14	15 - 560
TOC, mg/l	5 - 6	20 - 40
Fe, mg/l	200 - 550	<0.02
Mg, mg/l	65 - 90	60 - 300
Pb, mg/l	0.2 - 0.6	<0.06 - 0.3

* Coal from eastern Kentucky
** Coals from Utah, Wyoming and Montana

Overall, it is predicted that both eastern coal slurries and western coal slurries will require treatment before discharge. Problems with chlorinating the filtrates and producing THM's is of greater concern for western coal slurries than for eastern coal slurries because of the higher TOC levels observed in western slurries.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The water quality characteristics of a coal slurry involving eastern coal were evaluated. Eastern Kentucky coal and tap water were slurried and continuously pumped through a pilot-plant closed-loop pipeline for ten days. Coal slurry samples were withdrawn at seven different times and were filtered and analyzed for twenty-nine water quality parameters, including fifteen metals. Two runs were completed without a corrosion inhibitor and two runs were completed with the addition of a corrosion inhibitor. From the results obtained in this research, the following conclusions were reached.

1. The water quality characteristics of a coal slurry can vary widely, depending upon the coal used and the use of a corrosion inhibitor.

2. Dissolved oxygen levels will drop quickly in a pipeline and will remain near zero.

3. Immediately after filtering a coal slurry, which is void of oxygen, a precipitate may form in the filtrate, depending upon the amount of dissolved metals present, particularly iron.

4. Coal slurry filtrates are expected to be free of color.

5. Eastern coal slurries will contain high sulfate concentrations, which will be related to the percent sulfur in the coal. Corrosion inhibitors cause more sulfates to become soluble.

6. Chlorides leach from coal into transport waters.

7. Total dissolved solids and conductivity levels are high for eastern coal slurries and the addition of a corrosion inhibitor will increase these levels.

8. Coal slurries will turn from an oxidizing environment to a reducing environment after 1-2 days in the pipeline.

9. The pH will drop initially in a coal slurry, depending upon the alkalinity present and the percent sulfur in the dry coal, but will rise to near neutral levels after ten days.

10. Acidity is expected to be high in this eastern coal slurry. The level is a function of sulfates and pH.

11. Alkalinity is expected to be relatively low in eastern coal slurries. Corrosion inhibitors contribute greatly to alkalinity.

12. Total organic carbon level was very low for this particular coal slurry. TOC appears to increase as pH increases.

13. Trihalomethane formation potential was low for this particular coal slurry.

14. For this particular eastern coal, its slurry water is expected to contain very low levels of phenols.

15. Metals will leach from coals into transport waters and will attain levels which require treatment. The pH of a slurry will affect the solubilities of most metals. The major metals

contained in this particular coal slurry were iron, magnesium, lead and aluminum.

16. The addition of a corrosion inhibitor will increase the concentrations of many parameters. Metals concentrations will decrease depending upon the pH.

Recommendations

The water quality characteristics of eastern coal slurries do not appear to present any major problems which cannot be corrected by treatment in terms of water usage after pipelining.

Further study is warranted for different eastern coals to more accurately predict the final water quality. As seen in the Literature Review (Chapter II), each coal slurry is unique. Coals from other mines in the eastern United States should be tested. Further data is required to support the conclusions reached thus far.

Different corrosion inhibitors should be tested to observe any beneficial effects. The treatability of coal slurries should be investigated. The parameters of concern in this study (metals, sulfates) are treatable, however, it may be costly to remove them. Economical and effective treatment methods should be investigated in the near future if coal slurry pipelines are expected to go into operation soon.

REFERENCES

1. Anderson, Orson L.; Rogozen, Michael B.; Margler, Lawrence W.; Mankiewicz, Paul; and Axelrod, Marc H. Water Pollution Control for Coal Slurry Pipelines. Prepared for the U.S. Department of Energy. NTIS SAI-068-79-516. Springfield, VA: National Technical Information Service, 1978.

2. Standard Methods for the Examination of Water and Wastewater. 14th ed. Washington, D.C.: American Public Health Association, 1975.

3. Margler, Lawrence W., and Rogozen, Michael B. "Effects of Coal Slurry on Wastewater Bacteria and Bacteriolophase." Journal Water Pollution Control Federation 52 (January 1980): 53-58.

4. Moore, James W. Water Quality Aspects of Coal Transportation by Slurry Pipeline. Fayetteville, AR: Arkansas Water Resources Research Center, University of Arkansas, August 1980.

5. Moore, James W. "Water Quality Aspects of Coal Transportation by Slurry Pipeline." Proceedings of the Fourth International Technical Conference on Slurry Transportation, Las Vegas, Nevada, March 28-30, 1979, Washington, D.C.: Slurry Transport Association, 1979.

6. U.S. Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Washington, D.C.: Office of Technology Transfer, U.S. Environmental Protection Agency, EPA-625/6-74-003, 1974.

7. Moore, James W. "Quality Characteristics of Slurry Wastewater Resulting from the Slurry Pipelining of Eastern Coal." Proceedings of the Fifth International Technical Conference on Slurry Transportation, Las Vegas, Nevada, March 26-28, 1980, Washington, D.C.: Slurry Transport Association, 1980.

8. Moore, James W. "Water Quality Aspects of Coal Transportation by Slurry Pipelining of Eastern Coal on Water Quality." Proceedings of the Sixth International Technical Conference on Slurry Transportation, Las Vegas, Nevada, March 24-27, 1981, Washington, D.C.: Slurry Transport Association, 1981.

9. Manahan, Stanley E.; Godwin, Judith A.; and Shinn, Michael H. Quality and Treatment of Water Involved with Coal Slurry Transport by Pipeline. Prepared for the Missouri Water Resources Research Center, University of Missouri. NTIS PB80-160724. Springfield, VA: National Technical Information Service, 1980.

10. Peavy, Howard S.; Jennings, P.W.; and Murgel, George A. Water Pollution Potential of Coal-Slurry Pipelines. Prepared for Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Final report, Contract No. R-805176-01. Reproduced by Montana State University, November 1980.

11. Peavy, Howard S. Water Pollution Potential of Coal-Slurry Pipelines, Project Summary. Cincinnati, OH: Center for Environmental Research Information, U.S. Environmental Protection Agency, EPA-600/57-81-082, June 1981.

12. Peavy, Howard S. "Water Quality as a Factor in the Reuse and Disposal of Coal Slurry Water." Proceedings of the Seventh International Technical Conference on Slurry Transportation, Lake Tahoe, Nevada, March 23-26, 1982, Washington, D.C.: Slurry Transport Association, 1982.

13. Plummer, Alan H.; Jordon, Betty; Derammelarer, Ron; and Sandhu, Avtar. "Coal Slurry Dewatering Operations, Wastewater Treatability Studies." Proceedings of the Seventh International Technical Conference on Slurry Transportation, Lake Tahoe, Nevada, March 23-26, 1982, Washington, D.C.: Slurry Transport Association, 1982.

14. Sandhu, Avtar Singh, and Gandhi, Ramesh L. "Water Quality Simulation for the Design of the ETSI Wastewater Treatment Facilities." Proceedings of the Seventh International Technical Conference on Slurry Transportation, Lake Tahoe, Nevada, March 23-26, 1982, Washington, D.C.: Slurry Transport Association, 1982.

15. Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater: Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency. Port City Press: Public Health Association, 1981.

16. Bosshart, Robert E.; Price, Andrea A.; and Ford, Charles T. Evaluation of Coal Cleaning on Fugitive Elements - Part II, Analytical Methods. Washington, D.C.: U.S. Department of Energy, C00-4427-35, 1980.

17. Roddy, M.R. C.D. McIntosh Power Plant, Lakeland Utilities Company, Lakeland, Florida. Personal communication, November 1983.

18. Snoeyink, Vernon L., and Jenkins, David. Water Chemistry. New York: John Wiley and Sons, Inc., 1980.